Metals and Ceramics Division

CERAMIC TECHNOLOGY PROJECT
SEMIANNUAL PROGRESS REPORT FOR
OCTOBER 1993 THROUGH MARCH 1994

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Project Manager

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CERAMIC TECHNOLOGY PROJECT SEMIANNUAL PROGRESS REPORT
FOR OCTOBER 1993 THROUGH MARCH 1994

SUMMARY

The Ceramic Technology Project was originally developed by the Department of Energy's Office of Transportation Systems (OTS) in Conservation and Renewable Energy. This project, part of the OTS's Materials Development Program, was developed to meet the ceramic technology requirements of the OTS's automotive technology programs.

Significant accomplishments in fabricating ceramic components for the Department of Energy (DOE), National Aeronautics and Space Administration (NASA), and Department of Defense (DoD) advanced heat engine programs have provided evidence that the operation of ceramic parts in high-temperature engine environments is feasible. However, these programs have also demonstrated that additional research is needed in materials and processing development, design methodology, and data base and life prediction before industry will have a sufficient technology base from which to produce reliable cost-effective ceramic engine components commercially.

An assessment of needs was completed, and a five-year project plan was developed with extensive input from private industry. In July 1990, the original plan was updated through the estimated completion of development in 1993. The original objective of the project was to develop the industrial technology base required for reliable ceramics for application in advanced automotive heat engines.

During the course of the Ceramic Technology Project, remarkable progress has been made in the development of reliable structural ceramics. However, further work is needed to reduce the cost of ceramics to facilitate their commercial introduction, especially in the highly cost-sensitive automotive market. To this end, the direction of the Ceramic Technology Project is now shifting toward reducing the cost of ceramics to facilitate commercial introduction of ceramic components for near-term engine applications. In response to extensive input from industry, the plan is to extend the engine types which were previously supported (advanced gas turbine and low-heat-rejection diesel engines) to include near-term (5-10 years) applications in conventional automobile and diesel truck engines. To facilitate the rapid transfer of this technology to U.S. industry, the major portion of the work is being done in the ceramic industry, with technological support from government laboratories, other industrial laboratories, and universities.

A systematic approach to reducing the cost of components is envisioned. The work elements are as follows: economic cost modeling, ceramic machining, powder synthesis, alternative forming and densification processes, yield improvement, system design studies, standards development, low-expansion ceramics, and testing and data base development.

This project is managed by ORNL for the Office of Transportation Technologies, Propulsion System Materials Program, and is closely coordinated with complementary ceramics tasks funded by other DOE offices, NASA, DoD, and industry. A joint DOE and NASA technical plan has been established, with DOE focus on automotive applications and NASA focus on aerospace applications. A common work breakdown structure (WBS) was developed to facilitate coordination. The work described in this report is organized according to the following WBS project elements:

0.0 Project Management and Coordination

1.0 Materials and Processing

- 1.1 Monolithics
- 1.2 Ceramic Composites
- 1.3 Thermal and Wear Coatings
- 1.4 Joining
- 1.5 Ceramic Machining

2.0 Materials Design Methodology

- 2.1 Modeling
- 2.2 Contact Interfaces
- 2.3 New Concepts

3.0 Data Base and Life Prediction

- 3.1 Structural Qualification
- 3.2 Time-Dependent Behavior
- 3.3 Environmental Effects
- 3.4 Fracture Mechanics
- 3.5 Nondestructive Evaluation Development

4.0 Technology Transfer

- 4.1 Technology Transfer

This report includes contributions from all currently active project participants. The contributions are arranged according to the work breakdown structure outline.

0.0 PROJECT MANAGEMENT AND COORDINATION

D. R. Johnson
Oak Ridge National Laboratory

Objective/scope

This task includes the technical management of the project in accordance with the project plans and management plan approved by the Department of Energy (DOE) Oak Ridge Operations Office, and the Office of Transportation Technologies. This task includes preparation of annual field work proposals, initiation and management of subcontracts and interagency agreements, and management of ORNL technical tasks. Monthly management reports and bimonthly reports are provided to DOE; highlights and semiannual technical reports are provided to DOE and program participants. In addition, the program is coordinated with interfacing programs sponsored by other DOE offices and federal agencies, including the National Aeronautics and Space Administration (NASA) and the Department of Defense (DoD). This coordination is accomplished by participation in DOE and NASA joint management meetings, annual interagency heat engine ceramics coordination meetings, DOE contractor coordination meetings, and DOE Energy Materials Coordinating Committee (EMaCC) meetings, as well as special coordination meetings.

1.0 MATERIALS AND PROCESSING

INTRODUCTION

This portion of the project is identified as project element 1.0 within the work breakdown structure (WBS). It contains five subelements: (1) Monolithics, (2) Ceramic Composites, (3) Thermal and Wear Coatings, (4) Joining, and (5) Ceramic Machining. Ceramic research conducted within the Monolithics subelement currently includes work activities on low cost Si_3N_4 powder, green state ceramic fabrication, characterization, and densification, and on structural, mechanical, and physical properties of these ceramics. Research conducted within the Ceramic Composites subelement currently includes silicon nitride and oxide-based composites. Research conducted in the Thermal and Wear Coatings subelement is currently limited to oxide-based coatings and involves coating synthesis, characterization, and determination of the mechanical and physical properties of the coatings. Research conducted in the Joining subelement currently includes studies of processes to produce strong, stable joints between zirconia ceramics and iron-base alloys. As part of an expanded effort to reduce the cost of ceramic components, a new initiative in cost effective machining has been started.

A major objective of the research in the Materials and Processing project element is to systematically advance the understanding of the relationships between ceramic raw materials such as powders and reactant gases, the processing variables involved in producing the ceramic materials, and the resultant microstructures and physical and mechanical properties of the ceramic materials. Success in meeting this objective will provide U.S. companies with new or improved ways for producing economical, highly reliable ceramic components for advanced heat engines.

1.1 MONOLITHICS

1.1.2 Silicon Nitride

Characterization of Attrition Milled Silicon Nitride Powder

S. G. Malghan, P. T. Pei, and D. B. Minor (National Institute of Standards and Technology)

Objective/Scope

Currently, the starting materials in the manufacture of silicon nitride ceramic components are fine powders. These fine sized powders tend to form agglomerates due to the Van der Waals attractive forces. For improved reliability in the manufacture of ceramic components, the agglomerates in the powders should be eliminated since they form defects. In addition, the powders should have an appropriate range of size distribution and specific surface area for achieving a near-theoretical density of the ceramic after densification. These factors necessitate the use of powder milling as one of the major powder processing unit operations. Therefore, milling of powders is an integral unit operation in the manufacture of silicon nitride components for advanced energy applications. The production and use of these powders require the use of efficient milling techniques and understanding of characteristics of the milled powders in a given environment. High energy attrition milling appears to offer significant advantages over conventional tumbling and vibratory mills.

The major objectives of this project are: 1. establish repeatability of particle size distribution and other relevant characteristics of slurries milled in a high energy agitation mill (HEAM); 2. determine processing and densification characteristics of powders milled in HEAM; and 3. compare properties of powder, and resulting ceramic obtained by milling in the HEAM vs. vibratory ball mill in a collaborative project with Norton Company.

Technical Progress

We have examined data on materials, milling process, and measurement processes. Under materials, silicon nitride, yttria, and ammonium polymethacrylate have been examined. In the milling process, since most of the parameters were held constant, operator induced changes are the main source of variability. Finally, we have examined repeatability in the measurements of particle size distribution, specific surface area, and electrokinetic sonic amplitude. The data resulting from this analysis are being summarized to obtain overall assessment of repeatability and major sources of deviations that affect the milling results. A technical paper is being prepared to summarize these findings.

One of the tasks under this project was to obtain an evaluation of milled slurries by densification of green compacts and measurement of mechanical properties. Silicon nitride powders containing 4% yttria were milled at NIST in the high energy agitation ball mill to a nominal specific surface area of 12 m²/g and a mean particle size distribution of 0.55 μ m. The slips in as-milled condition were shipped to Drs. S. J. Lombardo and V. K. Pujari at St. Gobain-Norton Company. The slurries from two different tests were pressure cast and freeze-dried in

accordance with their established procedures. The freeze-dried samples were iso-pressed. It should be noted that the agitation milled samples have significantly different properties compared to the conventional milled samples. The shape forming unit operations were not optimized for these slurries. The green samples were hot isostatically pressed, and subsequent evaluation of the mechanical properties was carried out at St. Gobain-Norton Company.

As reported previously, the green densities from the agitation milled slips were consistently in excess of 2.0 g/cm^3 . Often densities as high as 2.28 g/cm^3 were obtained. These densities are considered to be much higher than those obtainable from the conventional milled slips. The final properties of the ceramic were the following:

<u>Forming</u>	<u>MOR (MPa)</u>	<u>K_{1c} (MPa^{m1/2})</u>
CIP	725	5.7
Cast	691	4.4

As reported by Dr Lombardo, typical MOR values from their NCX-5102 are in the range of 800-900 MPa. The above reported values are certainly lower than those of NCX-5102. Considering the lack of optimization of the forming unit operations from these slips, the lower values are expected. Our future activities will focus on improving the formability of the agitation milled slips.

We have initiated a study to examine the aqueous surface chemistry of yttrium oxide powder as applied to its use as a sintering aid. A literature search was completed which showed that very little data are published on this subject. The available data indicate that yttrium oxide forms a highly unstable suspension in aqueous environment at high initial pH. The pH of 1-2 wt.% suspensions undergoes a continuous change over the time frame appropriate for milling suspensions. Two factors contributing to this change are not only the surface dissolution of yttria but also carbon dioxide adsorption. The dissolution of yttria appears to be not a problem until at least a pH of 6.0. There is a good amount of discussion and an overall lack agreement on the specifics of dominant species responsible for control of surface charge in alkaline pH range. We have conducted a detailed study of dissolution kinetics, adsorption of polymethacrylate dispersant, and dispersion characteristics of a yttria in aqueous suspensions. The primary measurements of surface chemistry have been conducted with electroacoustics, though a small amount of x-ray photoelectron spectroscopy studies are in progress. We plan to complete these studies and utilize them in the milling of silicon nitride powders.

A test to evaluate the HEAM was conducted by preparing a slip for gel casting. This test conducted in collaboration with Dr. Mark Janney was aimed at obtaining a high density slip. The specific goal was to attain a 80% solids by weight in the slip. The procedure used for milling in this test was developed at Dr. Janney's laboratory. Except for the use of the HEAM all other steps such as powder and surfactants

addition were the same as those practiced for gel casting suspensions preparation. The test ran fairly well until the end when the test had to be discontinued because the solids build up caused flow problems. A second test is planned in which the procedure will be modified to build the solids in a relatively shorter time so the overall milling time could be reduced to approximately 50 minutes. This is considered to be an important aspect of milling submicrometer powders since very little size reduction is required for powders such as SNE-10. The longer milling time tends to produce excessive heat in the slip without actually contributing to size reduction or deagglomeration.

Status of Milestones

On target.

Communications/Visits

None

Publications

None

Microwave Sintering of Silicon Nitride

J. O. Kiggans, T. N. Tiegs, and C. Davisson (Oak Ridge National Laboratory)

Objective/scope

The objective of this research element is to identify those aspects of microwave processing of silicon nitride that might (1) accelerate densification, (2) permit sintering to high density with much lower levels of sintering aids, (3) lower the sintering temperature, or (4) produce unique microstructures. The investigation of microstructure development is being done on dense silicon nitride materials annealed in the microwave furnace. The sintering of silicon nitride involves two approaches. The first approach comprises heating of silicon nitride and sialon powder compositions in the 2.45- or 28-GHz units. The second approach deals with using reaction-bonded silicon nitride (RBSN) as the starting material and is done entirely in the 2.45-GHz microwave furnace.

Technical highlights

Sintered Reaction-Bonded Silicon Nitride (SRBSN) - During the current reporting period, a series of experiments were performed using a Taguchi statistical array to determine the optimal processing conditions and sample compositions for nitridation and sintering of SRBSN. The variables that were tested are listed in Table 1. Note that for this Taguchi array, 12 runs were necessary. Since there were so many variables to be tested, nitridation and sintering of the samples was done by conventional heating. The final nitridation condition was 1450°C for 2 h in several flowing gas atmospheres. The final densification condition was 1800°C for 2 h under 0.1 MPa nitrogen with samples packed in Si₃N₄ packing powder.

Samples were weighed before and after the nitridation to determine the extent of nitridation. A portion of each sample was sliced following nitridation for X-ray analysis to determine the α -Si₃N₄ content. The density of each sample was determined following sintering using the Archimedes method.

Table 1 lists the silicon weight gain, the α -Si₃N₄ content, and the final sintered density value for each sample processed. Although it is obvious from this table that the Y₂O₃-SiO₂ sintering aids resulted in poor sintering in all cases in which they were used, other trends are more difficult to see. A statistical analysis was made of the values obtained for the nitridation, the α -Si₃N₄ content, and the final sintered density.

Table 2 summarizes the results of the analysis by listing the most optimal condition or composition for each variable that was tested. Table 2 also ranks the relative condition effect of each variable on a scale of weak, to moderate, to strong. One can see, for example, that a 1-h milling time was optimal for nitridation; however, it was listed as a weak effect since it was only slightly better than the 4-h milling treatment. Many important effects are summarized in this table. Plans are being made for other Taguchi array experiments to test other variables that may be important for the maximal nitridation and sintering of SRBSN.

In addition to the tests described above, experiments to optimize the microwave processing conditions for nitridation of silicon for SRBSN were also performed. The experimental array and results are shown in Table 3. One batch of

Table 1. Taguchi experimental design array for optimizing the powder processing conditions and composition for sintered reaction-bonded silicon nitride. Nitridation was done by conventional heating.
The design is an $L_{12} (2^{11})$ with 11 variables at 2 levels.

Test No.	Mill time (h)	Sinter aids	Sinter aids amt (wt %)	Metal additive	Metal additive content (wt %)	α -seed amt. (wt %)	Binder burnout atmosphere	Bisque fire atmosphere	Nitriding gas	Sample thickness (in.)	Green density (% TD)	Silicon weight gain (%)	α -Si ₃ N ₄ content (%)	Sintered density (% TD)
1	1	Y ₂ O ₃ -Al ₂ O ₃	12	Fe	0.5	10	Argon	Argon	5% He	0.375	58	61.3	34	97.0
2	1	Y ₂ O ₃ -Al ₂ O ₃	12	Fe	0.5	0	Air	Vacuum	No He	0.75	62	61.9	34	95.4
3	1	Y ₂ O ₃ -Al ₂ O ₃	9	Cr	2	10	Argon	Argon	No He	0.75	62	60.2	72	89.0
4	1	Y ₂ O ₃ -SiO ₂	12	Cr	2	10	Air	Vacuum	5% He	0.375	62	60.8	92	67.1
5	1	Y ₂ O ₃ -SiO ₂	9	Fe	2	0	Air	Argon	5% He	0.75	58	61.4	84	66.8
6	1	Y ₂ O ₃ -SiO ₂	9	Cr	0.5	0	Argon	Vacuum	No He	0.375	58	61.9	87	63.5
7	4	Y ₂ O ₃ -Al ₂ O ₃	9	Cr	0.5	10	Air	Vacuum	5% He	0.75	58	60.9	63	87.2
8	4	Y ₂ O ₃ -Al ₂ O ₃	9	Fe	2	0	Argon	Vacuum	5% He	0.375	62	62.2	43	90.6
9	4	Y ₂ O ₃ -Al ₂ O ₃	12	Cr	2	0	Air	Argon	No He	0.375	58	58.3	87	96.0
10	4	Y ₂ O ₃ -SiO ₂	9	Fe	0.5	10	Air	Argon	No He	0.375	62	60.0	93	67.1
11	4	Y ₂ O ₃ -SiO ₂	12	Cr	0.5	0	Argon	Argon	5% He	0.75	62	61.3	77	71.0
12	4	Y ₂ O ₃ -SiO ₂	12	Fe	2	10	Argon	Vacuum	No He	0.75	58	61.9	93	66.8

Table 2. Optimum powder processing conditions and composition for sintered reaction-bonded silicon nitride to maximize silicon weight gain, α -Si₃N₄ content (during nitridation), and sintered density.

Firing parameter	Optimum condition for maximum weight gain	Condition effect	Optimum condition for maximum α -Si ₃ N ₄ content	Condition effect	Optimum condition for maximum sintered density	Condition effect
Milling time	1 h	Weak	4 h	Moderate	1 h	Weak
Sintering aids	Y ₂ O ₃ -Al ₂ O ₃	Weak	Y ₂ O ₃ -Al ₂ O ₃	Strong	Y ₂ O ₃ -Al ₂ O ₃	Strong
Sintering aids amt.	9%	Weak	9%	Weak	12%	Strong
Metal additive	Fe	Moderate	Cr	Strong	Fe	Weak
Metal add. amt.	0.5%	Weak	2%	Strong	0.5%	Weak
α -Si ₃ N ₄ content	0%	Weak	10%	Weak	0%	Weak
Binder burnout	Vacuum	Moderate	Argon	Weak	Argon	Moderate
Bisque fire	Argon	Moderate	Air	Moderate	Air	Weak
Nitriding gas	5% He	Moderate	No He	Strong	5% He	Weak
Sample thickness	0.75 in.	Weak	0.375 in.	Weak	0.375 in.	Weak
Green density	62%	Weak	58%	Weak	62%	Weak

Table 3. Taguchi experimental design array for optimizing nitridation of silicon in a microwave furnace. The design is an $L_{12}(2^{11})$ with 11 variables at 2 levels.

Test No.	Ramp 1 °C/min	Ramp 2 °C/min	Ramp 3 °C/min	Hold time 1 (h)	Hold time 2 (h)	Hold time 3 (h)	Hold temp 1 (°C)	Hold temp 2 (°C)	Hold temp 3 (°C)	Sample thickness (in.)	Green density (% TD)	Silicon weight gain (%)	α -Si ₃ N ₄ content %	Sintered density (% TD)
1	1	0.5	0.3	1	1	1	1200	1325	1400	0.375	58	62.73	91	94.8
2	1	0.5	0.5	1	1	4	1250	1350	1450	0.75	62	62.25	33	93.9
3	1	0.5	2	4	4	1	1200	1325	1450	0.75	62	55.74	61	94.2
4	1	2	0.5	4	4	1	1250	1350	1400	0.375	62	62.07	89	94.9
5	1	2	2	1	4	4	1200	1350	1400	0.75	58	62.32	64	93.5
6	1	2	2	4	1	4	1250	1325	1450	0.375	58	62.19	71	94.2
7	5	0.5	2	4	1	1	1250	1350	1400	0.75	58	56.10	74	95.0
8	5	0.5	2	1	4	4	1250	1325	1400	0.375	62	61.82	70	95.8
9	5	0.5	0.5	4	4	4	1200	1350	1450	0.375	58	62.54	62	95.9
10	5	2	2	1	1	1	1200	1350	1450	0.375	62	58.57	71	95.4
11	5	2	0.5	4	1	4	1200	1325	1400	0.75	62	58.10	43	94.9
12	5	2	0.5	1	4	1	1250	1325	1450	0.75	58	61.30	46	93.3
Conf.	1	2	0.05	1	4	4	1250	1350	1400	0.375	58	62.24	86	94.1

material was used having a final composition of Si_3N_4 - 9 wt % Y_2O_3 - 3 wt % Al_2O_3 after nitridation. Samples of this composition have been shown to exhibit good mechanical properties in previous tests. Each thermal cycle consisted of a temperature ramp-up to 1100°C at $5^\circ\text{C}/\text{min}$, followed by a series of holds and temperature ramps as indicated in Table 3. The conditions were optimized for maximum nitridation weight gain and a confirmation run performed as shown in Table 3. The densification behavior of the samples was also determined by sintering in a conventional furnace at 1800°C for 2 h under 0.1 MPa nitrogen as shown in Table 3.

As with the previous Taguchi experiment, a statistical analysis was performed on the data. Table 4 lists the firing parameters studied along with the optimal condition and a ranking of weak, moderate, or strong. As an example, Table 4 shows that the $1^\circ\text{C}/\text{min}$ ramp 1 was optimal at a moderate level for maximal weight gain. This heating rate had a strong effect for the $\alpha\text{-Si}_3\text{N}_4$ content. However, a $5^\circ\text{C}/\text{min}$ ramp 1 was optimal for maximal sintering at a weak level. Other important data concerning heating rates, hold times, sample densities, and sample thickness values are shown in Table 4.

Scale-up of the SRBSN Process - To produce cost-effective ceramics for advanced heat engine applications, fabrication processes need to be appropriate for large-scale production of parts. The primary focus of the microwave sintering work during this working period has been the determination of the proper conditions for the scale-up of the SRBSN process using microwave heating.

In previous SRBSN-microwave processing studies, test samples were made in-house. One objective of the scale-up task was to find a provider of large numbers of pre-SRBSN green parts to eliminate this labor-intensive process. Injection-molded powder compacts of a bucket tappet geometry used in diesel engines were purchased from Cremer Forshchungsinstitut of Germany. The green bucket tappet samples consisted of a cup-like structure with the dimensions of 4.08-cm OD, 3.38-cm height, and with a 0.381-cm wall thickness. The buckets were bisque fired in nitrogen by the supplier to provide green strength for shipment. The samples had a nominal composition of silicon containing 30 wt. % Si_3N_4 and 5 wt. % each of Al_2O_3 and Y_2O_3 sintering aids. The green density of the buckets was $1.72 \text{ g}/\text{cm}^3$.

Nitridation and sintering of the bucket tappets was conducted in the ORNL 500-L cylindrical multimode cavity equipped with a 6-kW, 2.45-GHz power supply. Samples were placed into crucibles composed of boron nitride (BN), BN and silicon carbide (SiC), and RBSN, which were then insulated by a 5-cm layer of powder consisting of 83 wt % Si_3N_4 , 15 wt % BN, and 2 wt % Y_2O_3 . The crucibles and powder were held in 2.5-cm wall thickness alumina fiberboard box.

Two sets of microwave experiments were performed in this study. The first set involved three nitridation and sintering runs, in which parts were placed in one of three different BN cylindrical crucibles either in a single layer of four samples, two layers of four samples each, or three layers of seven samples each (Fig. 1). In the second series of microwave heating experiments, samples were processed in one of three crucibles, each designed to accommodate a single layer of nine samples, as shown in Fig. 2. The three crucibles were made of three different material combinations. Crucible 1 was made of all BN. Crucible 2 had a BN top and bottom and SiC sides. Crucible 3 consisted of an RBSN box with a removable RBSN lid and contained a bottom BN setter plate within the crucible.

Table 4. Optimum conditions for nitridation of silicon in a microwave furnace to maximize silicon weight gain, α -Si₃N₄ content, and sintered density.

Firing parameter	Optimum condition for maximum weight gain	Condition effect	Optimum condition for maximum α -Si ₃ N ₄ content	Condition effect	Optimum condition for maximum sintered density	Condition effect
Ramp 1	1° C/min	Moderate	1° C/min	Strong	5° C/min	Weak
Ramp 2	2° C/min	Weak	0.5° C/min	Weak	0.5° C/min	Weak
Ramp 3	0.5° C/min	Strong	2° C/min	Moderate	2° C/min	Weak
Hold time 1	1 h	Strong	4 h	Moderate	4 h	Weak
Hold time 2	4 h	Moderate	4 h	Weak	1 h	Weak
Hold time 3	4 h	Strong	1 h	Strong	4 h	Weak
Hold temp 1	1250° C	Moderate	1200° C	Weak	1200° C	Weak
Hold temp 2	1350° C	Weak	1350° C	Weak	1350° C	Weak
Hold temp 3	1400° C	Weak	1400° C	Strong	1400° C	Weak
Sample thickness	0.375 in.	Strong	0.375 in.	Strong	0.375 in.	Weak
Green density	58%	Moderate	58%	Moderate	62%	Weak

Fig. 1. Drawing showing the insulation package used for the first series of microwave processing experiments including (a) cross-section view of the entire package and (b) top view of the two possible sample arrangements used.

Fig. 2. Drawing of insulation package used in the second series of microwave processing experiments including (a) cross-section view and (b) top view.

After assembly of an appropriate sample package, the microwave furnace was evacuated and backfilled with nitrogen. Experiments were performed with flowing nitrogen. Both nitridation and sintering were performed in a single heating cycle of 20 h. The final sintering condition was 1800°C for 2 h. In the first set of experiments, the temperature of the samples was measured by a single type "C" thermocouple (TC) with a molybdenum sheath and a BN protective tip as shown in Fig. 1(a). Three type "C" TCs were used to measure temperatures in the second set of experiments. The TCs were located at 3-cm intervals at positions shown in Fig. 2. Comparative nitridation and sintering studies were conducted using a graphite resistance-heated furnace. Samples were loaded into BN and RBSN crucibles and then nitrided in flowing nitrogen and held at a final temperature of 1450°C for 2 h. After cooling to room temperature, the samples were covered with a 0.6-cm layer of Si₃N₄ powder containing 4 wt % Y₂O₃ and reheated in a graphite furnace. The sintering conditions were 1800°C for 2 h.

Samples from both the microwave and control groups were weighed before and after experiments. Sample locations and orientations within the crucibles were

recorded. Density determinations were made on sintered samples by the Archimedes method. Some sintered buckets from control and microwave tests were sliced into four sections of approximately equal thickness. The slices were made parallel to the base of the bucket tappet. The densities of each section were measured by the Archimedes method.

Table 5 shows a summary of the results from the first series of microwave processing runs along with the results of the two controls obtained from the conventionally processed samples. The four samples processed in run 1 had an average density of 3.26 g/cm^3 with a standard deviation of $\pm 0.004 \text{ g/cm}^3$. Figure 3 shows a photograph of an asreceived bucket tappet and one of the bucket tappets processed in this initial run. Run 2 in the microwave was a scale-up from four to eight samples. The samples were stacked in two layers of four samples each, as shown in Fig. 1(a). The average density was 3.27 g/cm^3 , with a standard deviation of $\pm 0.005 \text{ g/cm}^3$. The standard deviations of both microwave runs slightly exceeded that of the RBSN control but were lower than the BN control. The success of the 8-sample experiment run 2 led to a scale-up to a 3-layer, 21-sample experiment run 3. The average density for run 3 was 3.25 g/cm^3 , which was lower than the previous two experiments. More important, the standard deviation increased to $\pm 0.022 \text{ g/cm}^3$, which exceeded both control values. The densities of the 21 samples ranged from a high of 3.27 g/cm^3 to a low of 3.17 g/cm^3 . Analysis of the densities of the samples relative to their positions in the three-layer package showed that these differences in densities appeared to be due to temperature differences between the center and the edge of the crucible, since the samples in the center of each of the three layers sintered to higher densities than the samples on the peripheries.

Table 5. Densities obtained for SRBSN samples processed by microwave or conventional heating in experiment series 1.

Run No.	Processing method	Crucible	No. Layers	No. Samples	Avg dens (g/cm ³)	Std dev dens (g/cm ³)
1	Microwave	BN	1	4	3.26	0.004
2	Microwave	BN	2	8	3.27	0.005
3	Microwave	BN	3	21	3.23	0.022
4	Graphite furnace	BN	2	6	3.25	0.014
5	Graphite furnace	RBSN	1	9	3.26	0.003

Fig. 3. Photograph of bucket tappet parts as received and after processing by microwave heating.

In order to further investigate the suspected temperature problem associated with the microwave scale-up runs in the first set of experiments, and to see if susceptor crucibles might offer a solution, a second set of experiments was conducted. Table 6 shows the average densities and standard deviations obtained for the samples processed by microwave heating in the three types of crucibles tested, and also for samples heated in a graphite furnace in a RBSN crucible. Figure 4 shows the temperature profiles for the crucibles tested in the second set of experiments. The average density for the samples processed by microwave heating using a BN crucible was 3.27 g/cm^3 . The standard deviation of $\pm 0.006 \text{ g/cm}^3$ was double the value of the RBSN control group. The temperature measurements made in this run indicated that the center of the crucible (TC 1) was 12 to 14°C higher than the inner left edge of the crucible (TC 3). This temperature difference resulted in the variations in the densities of the samples as shown in Fig. 5(a). The next crucible tested for microwave processing of the bucket tappets had a BN bottom and top and SiC walls. The average density obtained was 3.28 g/cm^3 with a standard deviation of $\pm 0.003 \text{ g/cm}^3$. This standard deviation is one-half the value obtained with the BN crucible and is equal to the value obtained for the samples processed in the RBSN crucible in the graphite furnace. The block scatterplot shows that the data were

Table 6. Densities obtained for SRBSN samples processed by microwave and conventional heating in experiment series 2.

Processing method	Crucible type	Avg dens g/cm ³	Std dev dens g/cm ³
Microwave	BN	3.27	0.006
Microwave	BN-SiC	3.28	0.003
Microwave	RBSN	3.27	0.005
Graphite Furnace	RBSN	3.26	0.003

Fig. 4. Temperature profiles for experiment series 2 for the (a) BN-SiC crucible, (b) BN crucible, (c) BN-SiC crucible, and (d) RBSN crucible.

Fig. 5. Block scatterplot showing the densities (g/cm^3) of nine samples versus their positions in a three-by-three array, for samples processed by (a) microwave heating in a BN crucible, (b) microwave heating in a BN-SiC crucible, (c) microwave heating in a RBSN crucible, and (d) conventional heating in a RBSN crucible.

actually very uniform [Fig. 5(b)] with the exception of one sample. This sample was sawed into pieces which revealed an internal crack inside the base of the sample. The low-density value of the cracked sample was discarded when calculating the average and standard deviation in density for this group of samples. Temperature measurements indicated that a difference of 8°C existed between the center and inner edge of the BN-SiC crucible. The final crucible tested for use in microwave processing of the bucket tappets was an RBSN crucible. The average density achieved with this crucible was 3.27g/cm^3 , with a standard deviation of $\pm 0.005\text{g/cm}^3$. These values were approximately the same as the values obtained for microwave processing in the BN crucible. The thermal analysis showed a maximum of 9°C difference between the center and inside edge of the package. The block scatterplot [Fig. 5(c)] shows a density pattern only slightly better than that obtained for microwave processing in the BN crucible [Fig. 5(a)]. The poor performance of the RBSN crucible was not expected. Additional runs are being made

to confirm these data. In summary, the data from the three crucible runs indicated that the hybrid SiC-BN crucible produced the most uniform heating profile; however, more work is needed to define the exact material composition for the host crucible.

A second area of work has been the modeling of the temperature gradients inside a crucible used in a microwave processing experiment at the steady state sintering temperature of 1800°C. A customized version of the "T K Solver" software was used for the analysis. Information such as the thermal conductivity and emissivity values of the furnace, the samples, the insulation, and the interior crucibles at steady state temperature, as well as the dimensions of the various items, were entered into the program. The program estimated that a 10°C temperature difference would exist between the center and inside edge of a spherical BN crucible. This approximated closely our experimental result of 14°C. The initial modeling work showed that such studies may be valuable in providing information for experimental design. Further modeling experiments are being planned.

Comparisons were also made to determine the uniformity of individual samples processed by microwave and conventional heating in the previously described experiments. Table 7 shows that the uniformity of the densities obtained for slices from individual samples was comparable for samples processed by conventional and microwave heating. Thus, although it has been shown that temperature gradients can exist in the sample crucibles used in microwave processing runs, density variations did not appear to be a problem in individual samples.

Table 7. Densities of slices from SRBSN bucket tappet samples processed by microwave and conventional heating in different crucibles.

Processing method	Crucible type	Sample position	Density (g/cm ³)			
			Slice 1 ^c	Slice 2	Slice 3	Slice 4
Microwave	BN	Center ^a	3.28	3.28	3.28	3.28
Microwave	BN	Edge ^b	3.28	3.28	3.28	3.28
Microwave	BN-SiC	Center	3.28	3.28	3.28	3.28
Microwave	BN-SiC	Edge	3.27	3.28	3.27	3.27
Microwave	RBSN	Center	3.28	3.28	3.28	3.28
Graphite furnace	BN	Edge	3.28	3.28	3.27	3.27
Graphite furnace	RBSN	Edge	3.27	3.28	3.28	3.28

^aSample was located in the center of the crucible.

^bSample was located on the inside edge of the crucible.

^cSlice one was the top of the bucket tappet.

Development of a High Quality, Low Cost Silicon Nitride Powder

D. F. Carroll, G. A. Cochran, C. L. Conner, S. D. Dunmead, G. A. Eisman, J. Hwang, and A. W. Weimer (The Dow Chemical Company)

OBJECTIVE/SCOPE

The objective of this program is to scale a carbothermal nitridation process to the pilot plant level for the production of a high quality, low cost silicon nitride powder. The tasks of this program are designed to 1) determine the relationships between raw material precursors, reactor conditions and post-processing on the characteristics of carbothermal powder produced in the intermediate scale reactor, 2) scale the process to a pilot plant stage and 3) identify those characteristics which yield a sinterable powder that can be pressureless sintered into dense, high strength components. The results of the above tasks will be utilized in the latter stages of the program when high quality, low cost silicon nitride powder is produced in our pilot plant facility.

TECHNICAL PROGRESS**TASK 2.0 Process Development and Process Scale-up**

The process development and scale-up effort continued during this reporting period as detailed under Task 2. The objective of the task is to scale The Dow Chemical carbothermal process to produce silicon nitride at the pilot plant level. Within this reporting period, the program focused on powder synthesis fundamentals, optimization of key unit operations, and from the parts development effort, improvements in the powder based on feedback on critical powder properties as they relate to powder handling and processing. In addition, during this period powder and MOR test specimens were sent to Oak Ridge National Laboratory and AlliedSignal Ceramic Components as part of the program deliverable schedule.

Activities which took place under Task 2 addressed the unit operations associated with the pilot plant. The powder production campaigns carried out were meant to identify the challenges and problems associated with moving and handling solids specific to silicon nitride, assess the quality of the powder as it moves through the process, optimize key unit operations, develop an understanding of reactor control, and manufacture powder for both in and out-of-house commitments. During the campaigns, hundreds of pounds of powder were synthesized and evaluated (as outlined under Task 3) and provided material for evaluation purposes.

At the onset of the reporting period, attempts were made to determine if the pilot plant was capable of extended operating periods. Run trials of hundreds of hours of operation were planned and carried out. Results of such tests were deemed successful as the reactor and all other major unit operations could be operated upon demand for operating periods of up to approximately 450 hours. Run trials beyond this period were not attempted. As planned during the trials, certain key process variables were monitored and used to determine the stability of the process (as determined by the analytical characteristics of the product powder). Presented in Figure 1 is a run chart of the residual oxygen and carbon for the 450 hour campaign. The results, shown in Figure 1, indicate that after an initial lining out period, the process is capable of running for extended periods of time in a stable mode. Additional run trials of 192, 264, and 339 hours were carried out within the October 1993 - March 1994 time frame.

Figure 1
Residual Oxygen and Carbon vs. Time

A large effort was also carried out on the optimization of the burn-out cycle of excess carbon. The focus was primarily directed to developing a better understanding of the burn-out cycle at the pilot plant level while at the same time enhancing the equipment used in this step of the process. Equipment modifications were made for optimizing the gas composition during the burn-out of excess carbon. The equipment modifications were made in order to maintain a safe working environment. By using designed experimentation concepts, gas phase conditions were determined in order to achieve maximum burn-out rates without jeopardizing product powder quality. The results from the intermediate carbon burn-out evaluations were used as input for the larger trials. Operating variables, such as throughput, residual carbon, temperature, and gas composition, were evaluated in order to determine how they impact final product quality.

Additional pilot plant activity during the period included 1) assessment of the viability of utilizing new solids handling process equipment, 2) reduction of contamination sources, and 3) adding process control equipment to the pilot plant reactor. The details of the three activities are presented below.

Solids Handling

In an attempt to improve certain powder handling steps in the processes, in particular how a precursor powder is processed into one which is amenable to the Dow Chemical process, a powder processing trial was set up and carried out with a vendor. The test, designed to evaluate how the powder handles in the equipment, was carried out with pilot plant precursor. The material is currently being evaluated and will be re-incorporated into the process stream. As determined from the test, the processing rate during the trial was over an order of magnitude greater than current rates in our pilot facility. As a result, use of this equipment may offer the potential for increasing efficiency of our preprocessing operations.

Contamination

During the reporting period finished powder was found to be high in aluminum content. Although the concentration of this impurity varied from lot to lot, the quantity was determined to be well above the desirable limit (> 50 ppm Al) as shown in Figure 2. In fact, within the first couple of months of the reporting period product powder was deemed unusable because of Al contamination and, as a result, forced the effort into extending the synthesis campaigns. It was during this time that an extensive evaluation of the processing operations was carried out. After completion of a rigorous evaluation of the different unit operations for a source of contamination, it was determined that powder from non-silicon nitride trials had collected in previously unsuspected locations on one particular piece of equipment. After clean out of the contaminated sites, the unit was restarted and product powder assessed for metals content. The results indicate that the main sources of contamination have been removed and the aluminum levels are now below analytical detection limits.

Figure 2
Post Burnout Aluminum Levels vs. Time
(Prior to Decontamination)

In order to ensure a high purity product, the powder was monitored on a continuous basis throughout each run for metals and key powder properties. In addition to contamination issues, by use of continuous monitoring, it is possible to obtain control stability data on the process. A list of routinely analyzed metals can be found in Table I. Presented in Figures 3 and 4 are data related to such monitoring as carried out in the aforementioned 450 hr campaign. In Figure 3, the impurity level of the powder is presented whereas in Figure 4 the surface area data of the burned out powder are plotted. Although only data for calcium and iron are plotted, the powder was analyzed for all the metal impurities listed in Table I. Aside from the two metals reported, the rest were found to be below the detection limits of the analytical instrumentation.

Table I
Routine Metals Analyses

Element	Detection Limit (ppm)
Fe	10
Ca	15
Mg	100
Y	15
Al	50
K	5
Zr	50
Ta	70
Sr	20

Figure 3
Impurity Level (ppm) vs. Time
Calcium and Iron
450 Campaign

Figure 4
Surface Area of Product vs. Time
450 hr campaign

Process Control

During the months of December and January, the activities carried out under Task 2 focused on process improvements in the pilot plant. In particular, hardware improvements were made on the reactor control system in an effort to upgrade the dependability of the unit as well as to enhance the computer monitoring of key process variables. Since installation, the additional field instrumentation has enhanced the overall process and product quality by maintaining more consistent operating temperatures.

Powder (10 kg) produced in the pilot plant was sent to the contract monitor at MMES-Oak Ridge in November of this reporting period.

In December, approximately 25 kg of powder was sent to AlliedSignal Ceramic Components for an independent assessment of the product.

Task 3.1 Powder Characterization

The powders produced during this period were characterized as detailed under the powder analysis procedure developed at the onset of the contract (Task 3.1). The 10 kg of silicon nitride powder, produced in Task 2.0 and delivered to MMES in November, as well as the 25 kg sent to AlliedSignal were subjected to the analysis process. Results of the analytical tests of the two deliverable samples are summarized in Table II. The table also includes the powder specifications as outlined under the contract.

Table II
Analytical Properties

	10 kg MMES <u>Sample</u>	25 kg AlliedSignal <u>Sample</u>	<u>Program Goals</u>
Oxygen Content (wt.%)	1.80	1.68	<2.5
Carbon Content (wt.%)	0.48	0.46	<0.6
Surface Area (m ² /g)	10.0	10.44	5-20
Particle Size Distribution			
d10 (µm)	0.40		
d50 (µm)	0.78	.82	<0.8
d90 (µm)	2.28		
Impurities (ppm)*			
Al	112	ND	<1300
Ca	67	65	<1000
Cl	ND(10)	ND	<100
S	ND(20)	ND	<100
Mg	ND(100)	ND	<50
Fe	33	26	<2000
Na	ND(400)	ND	<10
K	ND(5)	ND	<10

*ND() - not detectable at detection limit indicated in parenthesis

In order to demonstrate the low halogen content of the Dow powders, F and Cl concentrations were measured by fast neutron activation analysis on the November powder deliverable. The results of these analyses indicated that fluorine and chlorine levels in our powder were below the detection limits of the technique (<50 ppm and < 3 ppm, respectively).

The analysis of the powder throughout the process, as already referenced (see Task 2), is a key element in understanding how the process is operating from a process control perspective. This is extremely important if high quality powder is to be routinely produced. The extensive testing, which includes x-ray fluorescence for metals, residual oxygen and carbon by combustion analysis (Leco), surface area (BET), particle size analysis by laser light scattering, and powder x-ray diffraction for alpha/beta phase content are carried out on the major unit operations as well as on all incoming raw materials. To further enhance the understanding of key powder characteristics on processing conditions, neutron activation, scanning electron and transmission electron spectroscopy are used in conjunction with other state-of-the-art surface science techniques.

Task 3.4 Suspension Development/Task 3.5 Greenware Formation and Part Densification

Efforts over the last six months have concentrated on determining the effects milling and post-milling variables on the quality of our slip-cast greenware and the properties of the final sintered parts for the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ sintering formulation

The effect of milling variables, such as speed and time, on the rheology of a 42 volume % solids slip were examined using a set of statistically designed experiments. The results of this study have shown that (1) longer milling times were effective in reducing slip viscosity, decreasing the particle size distribution, and increasing green strength, green density and sintered density of our components; (2) excessive milling speeds increased slip viscosities resulting in a slight reduction in green and sintered densities; (3) a combination of high milling speeds and long milling times increased casting time which resulted in undesirable greenware that warped and cracked during sintering. From this study, optimum milling conditions for the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ sintering formulation have been identified for future greenware fabrication in Task 3.5.

Post-milling variables such as greenware drying and dispersant/binder removal have also been examined. Preliminary results indicate that our slip-cast greenware (approximately 50 x 60 x 12-15 mm in size) is relatively insensitive to changes in the drying conditions (temperature, time, humidity, etc.). Dispersant/binder removal is most effective when the heating rate is slow enough to avoid rapid melt-down and evolution of gaseous species. An optimization of these parameters has enabled the fabrication of greenware which can be pressureless sintered without warping or cracking.

An experimental design was also conducted to optimize the sintering schedule for our carbothermal silicon nitride powders using the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ sintering formulation. This experimental design focused on a two-step pressureless sintering schedule with the goal of finding sintering conditions which can consistently densify our powder to >98% of theoretical density. For this study, a 87.9 vol% Si_3N_4 , 5.0 vol.% Y_2O_3 , 2.9 vol.% Al_2O_3 and 4.2 vol.% SiO_2 formulation was utilized. The sintering schedule was statistically varied to examine the effects of an initial 1600°C isothermal soak followed by a second isothermal soak ranging from 1650°C to 1815 °C for 0 to 12 hrs. Greenware for this study was produced using our baseline slip-casting procedure for the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ sintering formulation.. All specimens were pressureless sintered in a BN crucible in a flowing nitrogen atmosphere. The results indicated that a sintering window existed which could pressureless sinter Dow carbothermal powder to greater than 99% theoretical density. The highest sintered densities were obtained when an initial 1600°C isothermal soak was utilized. The sintered density as a function of sintering conditions can be seen in Figure 5. This plot contains the percent of theoretical density contours predicted by the experimental design as a function of the temperature and time of the second isothermal hold. Specimens sintered at ~1730-1750°C for greater than 7 hours could reach greater than 98% of theoretical density.

During this reporting period, slip cast greenware was also fabricated from the 10 kg lot of carbothermal powder sent to MMES in November of 1993. The greenware was slip-cast using our baseline procedure for the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ sintering formulation. These plates were then pressureless sintered into components for the mechanical property evaluation and deliverables required in Task 3.7. A total of 11 plates were sintered with an average density of $98.5 \pm 0.2\%$.

Figure 5. Percent of theoretical density contours as a function of the sintering temperature and time for the second isothermal step of the sintering cycle.

Task 3.6 Part Fabrication at AlliedSignal Ceramic Component Division.

In order to obtain an independent assessment of the carbothermal powder generated by the Dow Chemical process, the efforts detailed under this sub-task called for approximately 25-50 kilograms of powder produced in our pilot plant to be sent to AlliedSignal Ceramic Component Division. The powder was produced in November and sent in mid-December for evaluation.

Task 3.7 Part Characterization

The sintered plates produced in Task 3.5 from the same powder lot used in the 10 kg deliverable to MMES were machined into a total of ninety 3 x 4 x 45 mm flexure specimens for mechanical property analysis. Twenty-eight of these specimens were tested according to the ASTM C1161 standard for measuring four point bend strengths. The average fracture strength and Weibull modulus of this material was measured to be 788 ± 160 MPa and 5, respectively. The fracture strengths were found to be very close to the >800 MPa goal required by the contract. However, the Weibull modulus was unexpectedly lower than the required goal of the contract. Fractography analysis has indicated that the wide scatter in strength measurements was due to the presence of defects associated with greenware preparation. This result was not surprising since these plates were one of our first attempts to slip cast the $Y_2O_3-Al_2O_3-SiO_2$ formulation. It is expected that the improved milling/slip casting procedures recently defined in Task 3.4/3.5 will eliminate these defects and improve our average strength and Weibull modulus. As part of a January deliverable, twenty-five of these specimens were sent to MMES for their evaluation.

In order to increase the mechanical properties of components made with carbothermal powder and surpass the strength requirements of the contract (>800 MPa), an experimental design was also conducted to optimize the sintering conditions with respect to strength for the $Y_2O_3-Al_2O_3-SiO_2$ system. A series of plates were slip cast using carbothermal powder produced in our pilot plant reactor. These plates were pressureless sintered in a BN crucible under flowing nitrogen conditions. The sintering conditions were statistically varied using the two-step pressureless sintering cycle described in Tasks 3.4/3.5. The results of this study indicated that the sintering cycle had a significant effect on the mechanical properties of the material. By using the proper sintering cycle, average fracture strengths on the order of 850-875 MPa were obtained. The fracture strength dependence on the sintering conditions is shown in Figure 6. This plot contains that average strength contours predicted by the experimental design as a function of the temperature and time of the second stage of the isothermal sintering cycle. The highest average fracture strengths were obtained for those specimens sintered at the lowest temperatures and the longest times. Fractography analysis of the specimens is underway to determine the reason for this strength trend. Two sintering conditions were selected to confirm the predicted strengths by the experimental design model (points A and B in Figure 6). The average fracture strengths of these materials were measured to be 840 and 780 MPa, respectively. These measured values are in good agreement with the predictions of the experimental design model.

Figure 6. Average strength contours as a function of the sintering temperature and time for the second isothermal step of the sintering cycle.

STATUS OF MILESTONES

All milestones are on schedule.

COMMUNICATION/TRAVEL

A paper was presented at the International Silicon Nitride Conference '93 by Dr. C. Conner, Stuttgart, Germany. October, 1993.

A paper was presented at the 1993 Annual Automotive Technology Development Contractors' Coordination Meeting, Dearborn, MI., Oct. 1993, by Drs. D.F. Carroll and A.W. Weimer.

Glenn Eisman and Dick Stoesser traveled to Cocoa Beach, Florida in January to meet with Ray. Johnson, Susan Winslow of MMES, and Bob Schulz of the Department of Energy.

Drs. D.F. Carroll and C.L. Conner visited AlliedSignal Ceramics Components in February to review the status of the powder assessment program.

PATENT ACTIVITY

During this reporting period, ten patent disclosures were written which relate to the production of silicon nitride and its related powder properties.

PUBLICATIONS

The 1993 Contractor's Coordination Meeting Proceedings paper was submitted to SAE for publication in February.

Cost Effective Sintering of Silicon Nitride Ceramics (SIU-C)

D. E. Wittmer (Southern Illinois University)

Objective/Scope

The purpose of this work is to investigate the potential of cost effective sintering of Si_3N_4 through the development of continuous sintering techniques and the use of lower cost Si_3N_4 powders and sintering aids.

Technical Highlights**Task 1. Refine Economic Model and Design for Chosen Furnace Configuration**

This task was completed as reported in an earlier bimonthly.

Task 2. Continue evaluation of sintering parameters on properties of selected Si_3N_4 compositions**Continuous Sintering**

During this reporting period additional disks of A2Y6, A2Y8, A2Y8 with 5 wt.% $\beta\text{-Si}_3\text{N}_4$ seed, and A2Y6 with 5 wt.% $\beta\text{-Si}_3\text{N}_4$ seed were prepared by turbomilling and pressure casting. Some of these disks were sintered at Centorr/Vacuum Industries in the Model 6-BF belt furnace with a modified graphite hot-zone. Sintering took place at 1700°C and 1725°C for 90 min. All of the compositions sintered to near theoretical density. The physical properties (flexural strength and fracture toughness) of the successfully sintered compositions were determined and compared to the same compositions previously sintered in the belt furnace with a tungsten hot-zone. Preliminary strength data was somewhat inconclusive. The major effects associated with sintering in the belt furnace with the graphite hot-zone appears to be higher weight loss and greater reaction layer thickness. These effects will be investigated in more detail in the prototype belt furnace as part of Task 4. The polished test bars used for fracture toughness evaluation have been microwave plasma etched and the microstructures are presently being examined by SEM. XRD analyses of the sintered compositions will also be made to determine if hot-zone type has any detectable influence on the $\alpha \rightarrow \beta\text{-Si}_3\text{N}_4$ conversion.

The CVI Model 6-BF belt furnace with the tungsten hot-zone was also used to finish the original matrix of sintering trials for A2Y6, A4Y6, and A2Y8 UBE E-10 Si_3N_4 compositions with and without $\beta\text{-Si}_3\text{N}_4$ seeding. The sintering temperatures of 1675, 1725 and 1750 °C for sintering times of 90 min and 1700 °C for sintering times of 30, 60 and 90 min were completed. The sintered disks

are presently being machined into test bars for flexural strength and fracture toughness measurements. Following physical property measurements, plasma etched surfaces will be observed by SEM and optically to perform image analyses on the microstructures.

High Temperature Testing

The power supply for the high-temperature testing system has been installed and the hardware for holding the furnace in place on the loading platform has been modified. The alumina rams for supplying the load to the high-temperature flexural fixture were chipped during installation and are being remachined. The furnace system had also been redesigned to allow for better access to the testing fixture. A second bench top testing machine dedicated to elevated temperature testing has been ordered with matching funds from SIU-C. This will allow the measurement of high-temperature flexure and creep without tying up the testing machine used for room-temperature properties. This second tester should be installed about the time as materials are available for elevated temperature testing. The furnace for use in these measurements was donated by CVI and the power supply was purchased with matching funds from SIU-C.

Improved Processing

A new procedure for "rapid" drying of pressure cast forms was developed and appears to work very well. The basis of this procedure is to place the as-cast forms in a vacuum oven over a dish containing water. After equilibrium is reached in the oven under ambient pressure and temperature, the oven temperature is slowly increased to 120°C and a very slight vacuum purge is started. As dictated by the ideal gas law, a temperature-pressure cycle is initiated as moisture is drawn from the system. This cycle is repeated as the relative humidity gradually decreases to zero and the forms are completely dry. With this procedure it was possible to dry the forms in 4 days, compared to our previous slow drying methods, which took 3-4 weeks and often produced cracked forms. This new drying procedure has produced disks without cracks in the green processed disks. Following isopressing, several of these disks were sintered in the belt furnace at Centorr/Vacuum Industries (CVI) without the problems typically associated with rapid drying; ie. none of the disks cracked or displayed severe warpage. The physical properties will be measured and the microstructures will be analyzed during the next reporting period to determine if there are any observable differences which can be related to the new drying procedure.

Work was also completed during this reporting period involving the influence of processing temperature and solids loading on the viscosity of UBE

E-10 and Starck LC-12SX Si_3N_4 with and without the addition of 2% Al_2O_3 and 8% Y_2O_3 . It is clear from the results that the powder formation method has a strong influence on the slurry behavior as a function of temperature. The addition of sintering aids produced a reduction in the viscosity for both Si_3N_4 powders and had a more pronounced effect at higher solids loading.

Task 3. Continue Evaluation of Low Cost Si_3N_4 Powder

The primary goal of this task will be to work with the low cost Si_3N_4 powder presently being produced by Dow Chemical Company, under contract to DoE through Martin Marietta Energy Systems, Inc.. Samples of the Si_3N_4 powder were originally scheduled to be available from Dow sometime in January of 94, however it has been decided that ORNL will decide how the powders will be distributed. Once powders are received, A4Y6 and A2Y6 formulations using these powders will be processed by turbomilling, pressure filtration, and belt sintering, in collaboration with Dow Chemical personnel. The physical properties will then be determined and compared with results obtained previously from other Si_3N_4 powders.

Task 4. Design and Construct Prototype Belt Furnace

During this reporting period, additional design work for the furnace and power system was completed by CVI as part of their matching contribution to this program. Preliminary and final drawings of the furnace have also been completed and reviewed at SIU-C. SIU-C issued a subcontract to CVI for construction of the prototype belt furnace, however construction of the furnace could not begin until funds for the construction of the furnace were made available. The issuance of these funds was delayed by the purchasing division of Martin Marietta for unknown reasons, and then delayed additionally by SIU-C. Because of the nature of the subcontract between SIU-C and CVI, SIU-C purchasing was required to receive approval from the Executive Committee of the Board of Trustees for SIU-C. This delayed the issuance of payment to CVI an additional 8 weeks. At the end of this reporting period, payment was made to CVI which has allowed them to order materials for furnace construction. It is anticipated that there will be no further delays and furnace delivery can be expected in late October or early November, with installation completed prior to the end of the calendar year. Because of these events the milestone for this task will need to be adjusted accordingly.

Status of Milestones

1.	Refine Economic Model and Design for Chosen Furnace Configuration	Completed

2.	Continue Evaluation of Sintering Parameters on Properties of Selected Si_3N_4 Compositions	On Schedule
Continuing
3.	Continue Evaluation of Low Cost Si_3N_4 Powders	On Schedule
Continuing
4.	Design and construct prototype belt furnace	Delayed

Communications/Visits/Travel

D. E. Wittmer to Dearborn, MI to present research results at the Annual Contractors Coordination Meeting, October 18-21, 1993.

V. A. Knapp, J. J. Conover, and B. Rodely to Cocoa Beach, FL Jan. 9-14, 1994 to present results of research.

D. Wittmer to CVI, Nashua, NH during March 14 -18th to complete sintering trials and discuss construction of prototype belt furnace with Charles W. Miller.

Problems Encountered

Funds for the construction of the prototype belt furnace were delayed by MMES and SIU-C which has resulted in rescheduling the completion of Task 4 to the end of the calendar year.

Publications

Dale E. Wittmer, Joseph J. Conover, and Vincent A. Knapp of Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr. of Centorr Furnaces/Vacuum Industries, Nashua, NH, "Cost Effective Sintering of Si_3N_4 ," 1993 CCM Proceedings, Dearborn, MI, October 18-21, 1993.

Dale E. Wittmer, Joseph J. Conover, and Vincent A. Knapp of Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr. of Centorr Furnaces/Vacuum Industries, Nashua, NH, "Cost Effective Sintering of Si_3N_4 ," SAE Publication, submitted for publication.

Vincent A. Knapp, Dale E. Wittmer, and Joseph J. Conover Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr. of Centorr Furnaces/Vacuum Industries, Nashua, NH, "Microwave Plasma Etching of Si_3N_4 ," Ceramic Engineering and Science Proceedings, submitted for publication.

Presentations

Dale E. Wittmer, Joseph J. Conover, and Vincent A. Knapp of Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr. of Centorr Furnaces/Vacuum Industries, Nashua, NH, "Cost Effective Sintering of Si_3N_4 ," 1993 Contractors Coordination Meeting, Dearborn, MI, October 18-21, 1993.

Vincent A. Knapp, Dale E. Wittmer, and Joseph J. Conover Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr. of Centorr Furnaces/Vacuum Industries, Nashua, NH, "Microwave Plasma Etching of Si_3N_4 ," 18th CCAC, Cocoa Beach, FL Jan. 9-14, 1994.

Joseph J. Conover, Dale E. Wittmer, and Vincent A. Knapp, Southern Illinois University, Carbondale, IL and Charles W. Miller, Jr., Centorr Furnaces /Vacuum Industries, Nashua, NH, "Microstructural Enhancement of Si_3N_4 ," 18th CCAC, Cocoa Beach, FL Jan. 9-14, 1994.

Cost Effective Process Silicon Nitride Engine Components

Garry Garvey (Golden Technologies Company, Inc.)

OBJECTIVE/SCOPE:

The objective of this work is to develop a low-cost process for the manufacture of high quality ceramic engine components based on sintered reaction bonded silicon nitride technology. The work shall comprise three technical tasks including materials selection, process development, and property evaluation. The material property goal for this work phase is a mean RT 4-point flexure strength of 525 MPa with Weibull Modulus equal to 15.

BACKGROUND

The commercialization of silicon nitride engine components requires that reliable, high strength silicon nitride material be available at a cost effective price. Today, many suppliers offer high strength and reliable silicon nitride. However, this material is very costly to produce due to high raw material and high processing costs. Typical silicon nitride powders range in price from \$15.00 to \$70.00 per pound. Sintering aides for silicon nitride are equally expensive. Yttria ranges from \$20.00 to \$60.00 per pound. The use of silicon as a raw material for sintered reaction bonded silicon nitride (SRBSN) can produce raw material savings, however, the current commercial practice of non-aqueous milling adds substantially to the processing costs.

In terms of the cost of thermal processing, the current practice of over-pressure sintering of silicon nitride requires substantial capitalization compared to ambient pressure sintering. It also requires a batch type approach to sintering. Both aspects of sintering add to the product costs.

Ideally, silicon nitride should be sintered at a minimum temperature at ambient pressure in a continuous mode.

Coors Ceramic Company / Golden Technologies Company has an executed License and Commercialization Agreement to license patents related to silicon nitride technology from Eaton Corporation. This technology is based on the aqueous processing of silicon metal to produce high quality SRBSN and promises to result in reducing the cost of silicon nitride parts.

This period, effort has focused primarily on determining the scalability and reproducibility of the overall process.

Process Scalability / Reproducibility

In order to determine the reproducibility of the overall process, a pilot scale (125 pounds/run) procedure has been developed, documented, and strictly repeated a total of six times. These six powder samples were nitrided and sintered on at least three different occasions. The densities, used as a measure of process reproducibility, are reported in the following table:

Densities of 6 Powder Samples						
Sinter Run #	532-103A	532-107	532-109A	532-126	532-128 (1)	532-128 (1)
1	3.31	3.30	3.31			
2	3.31	3.33	3.29	3.30	3.35	3.33
3	3.33	3.28	3.29	3.31	3.34	3.33
4	3.30	3.30	3.30	3.31	3.34	3.34

Dry Press Development:

Through manipulation of binder composition and dry pressing parameters, high density dry pressed parts have been obtained. Typical dry pressed densities greater than 99% of theoretical have been recorded. The average MOR strength of 100 bars was determined to be 96.6 kpsi (680 MPa) with a standard deviation of 6.7 kpsi (46 MPa).

Analysis of Section Cut from Industrial Parts

GTC manufactured parts in the geometry of a commercial cam follower roller (1.5" OD x 0.87" ID x 1.00" high). MOR test specimens were cut from these parts and tested for strength. Results indicated a strength of 670 ± 55 MPa (97 ± 8 ksi). A maximum strength of 863 MPa (125 ksi) was noted.

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SRBSN

# of Specimens Cut	=	8
Avg. Strength (MPa)	=	678
Std. Deviation (MPa)	=	60
Coefficient, (%)	=	9
Max. Strength (MPa)	=	758
Min. Strength (MPa)	=	580

Competitive Si_3N_4

# of Specimens Cut	=	5
Avg. Strength (MPa)	=	643
Std. Deviation (MPa)	=	40
Coefficient, (%)	=	6
Max. Strength (MPa)	=	694
Min. Strength (MPa)	=	605

CREDITS:

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Ceramic Technology Project of the Propulsion System Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

1.1.4 Processing of Monolithics

Improved Processing

V.K. Pujari, D.M. Tracey, M.R. Foley, A.B. Hardy, S.J. Lombardo, P.J. Pelletier, L.C. Sales, R.L. Yeckley (Norton Company)

OBJECTIVE/SCOPE

The goals of this contract are to develop and demonstrate significant improvements in processing methods, process controls, and nondestructive evaluation (NDE) which can be commercially implemented to produce high reliability silicon nitride components for advanced heat engine applications at temperatures to 1370°C. Achievement of these goals shall be sought through:

- Reliability optimization of aqueous colloidal forming using highly loaded suspensions and glass encapsulated HIP'ing.
- Application of the high reliability colloidal processing technique to a gas pressure sinterable (GPS) composition.
- Demonstration of representative complex component fabrication in both the HIP and GPS systems.

TECHNICAL HIGHLIGHTS

TASK 1: Forming Using Highly Loaded Suspensions and HIP'ing

i) Density Gradient Reduction

A series of experiments were conducted to determine the effect of slip, mold and casting characteristics on the green compact. The objective of the set of experiments was to evaluate and minimize density gradients in the cast components, and to examine how the control variables affect the performance variables. The control variables evaluated were the following:

Slip Variables

Surface area
Weight % solids

Mold Variables

Mold material

Casting Variables

Pressure profiles
Orientation of filtration surface (Up or down).

The performance variables examined in these experiments were:

Density of the green compact
 Density gradient (as measured by Hip'ed bending)
 Cracking during drying.

As indicated by Figures 1 to 4 green densities and density gradients have been correlated with surface area and weight percent solids of the slip. The casting rate of the slip has also been shown to have an effect on green densities and density gradients. The orientation of the filtration surface was a significant variable only at low weight percent solids since with low weight percent solids there is enhanced segregation of the slip. This results in an increased density gradient if the component is cast with the filtration surface on top (segregation and casting rate act in concert to increase the density gradient), and reduced if the filtration surface is toward the bottom (density gradients due to segregation and casting rate are counter-acting).

Process yield is reduced both by cracking during drying and by excessive bending during HIP'ing. These reject modes were found to depend upon green density in opposing fashions, with drying cracks more prevalent and bending less severe at higher green densities.

Figure 1: Green Density vs. Powder Surface Area

Figure 2: Green Density vs. Slurry Weight % Solids

Figure 3: Tensile Bar Runout vs. Powder Surface Area

Figure 4: Tensile Bar Runout vs. Slurry Weight % Solids

ii) Tensile Bar Fabrication and Testing

As a demonstration of the mechanical properties associated with the above process, buttonhead tensile specimens were tested for RT fast fracture strength and flexure specimens were tested for 1370°C stress rupture life. A post-HIP crystallization heat treatment was used in the production of the specimens to accentuate the HT mechanical behavior. In Phase I it was established that the crystallization step enhances HT strength as well as creep resistance, although the RT strength suffers somewhat due to this process step. The results of the current tests confirmed past experience. The flexure data are summarized in Table 1. The stress rupture (creep) tests were run at 300 MPa and 350 MPa. Exceptional creep resistance was found with 11 of 12 specimens surviving 200 hours at 1370°C.

Table 1

Test	Number of Specimen Tested	Average
Room Temp Fast Fracture	27	904.1 MPa
K _{IC}	24	6.59 MPa $\sqrt{m}$
1370 Fast Fracture	5	584.7 MPa
1370 Creep @ 300 MPa	6	6 survived 200 hours
1370 Creep @ 350 MPa	6	5 survived 200 hours, 1 failed at 46 hrs.

The NCX-5102 process developed in Phase I, Ref.1, was found to yield material with 1 GPa level tensile strength (997 MPa mean for n=320). This is in contrast to 700 MPa level tensile strengths of commercially available silicon nitride materials. A mean of 842 MPa was found for the tensile strength of 18 buttonhead specimens produced in the current experiments. The corresponding 2-parameter Weibull values are 895 MPa for characteristic strength and 10.1 for Weibull modulus. Compared to commercially available material, the 842 MPa mean strength is excellent. Compared to NCX-5102, 842 MPa represents a 16% mean strength reduction. This disparity can be viewed to be primarily a result of the crystallization step, a step that was not used in the NCX-5102 process.

iii) Establishing NDE Limits For Density Gradient Identification

A Si_3N_4 step wedge was used as a tool to determine the detection limits of Microfocus X-ray on density gradients. The material used for the step wedge was dense (HIP'ed) NCX-5102. The wedge was machined with 10 steps that varied in thickness from 3.60 mm to 3.81 mm. These changes in thickness simulated density differences of 0.2, 0.3, 0.4, 0.5, 0.8, and 1%. The operating parameters of the x-ray unit were optimized in order to get the best contrast and resolution. Using film radiography, a 0.5% density difference was found to be the detection limit for Microfocus X-ray.

TASK 2: High Reliability Colloidal Processing of GPS Composition

i) Aqueous Processing and Hydrolysis Control of MgO

Three methods have been identified to date to minimize the problems associated with the aqueous processing of magnesia containing slurries: temperature control, pH control and surfactant addition. Since previous results had demonstrated the importance of maintaining temperature control, a set of experiments was designed to assess the importance of pH and surfactant addition. A baseline silicon nitride plus yttria slurry was prepared and then cast after making additions of the magnesium sintering aids. As seen in Table 2, the baseline slurry attains a high green density upon casting, regardless of pH. Addition of magnesium sintering aid Mg(a) with surfactant, however, resulted in slurries which were too thick for casting. The addition of Mg(c) sintering aid resulted in a decrease in green density for both pH levels. The combination of Mg(c) plus surfactant at pH B yielded a cast body within 2% of the density of the baseline slurry. Thus, a combination of pH control and surfactant addition significantly reduces the problems associated with the processing of magnesium containing slurries.

Table 2: Green Densities Using Test Slurries

Sample	Green Density (g/cc)	
	pH = A	pH = B
Baseline ($\text{Si}_3\text{N}_4 + \text{Y}_2\text{O}_3$)	1.95	2.08
Baseline + Mg(a) + Surfactant	uncastable	uncastable
Baseline + Mg(c)	1.61	1.99
Baseline + Mg(c) + Surfactant	1.75	2.05

The results of these bench-top experiments were then scaled up to a 35 kg batch of slurry. As seen in Figure 5, the baseline silicon nitride plus yttria slurry attains a high green density. Addition of magnesium-containing sintering aids resulted in a decrease in green density relative to the baseline when no aging was allowed. There was indication, however, that a kinetic phenomenon was occurring and thus the slurries were allowed to age under continuous agitation. After four hours of aging, the green densities of the magnesium-containing slurries recovered to within 10% of the baseline value. Further aging of the slurry had no additional beneficial effect. Thus a scaled-up process has been developed whereby magnesium containing slurries can be cast to obtain bodies with acceptable green densities.

Figure 5: Cast Density vs. Aging Time of Test Slurries

ii) Gas Pressure Sintering (GPS) Optimization

Results of the most recent GPS cycle are provided in Table 3 below. The table contains flexure data on MOR bars machined from tiles. This sintering run examined the effect of the sintering bed and degradation of mechanical properties due to the reaction layer. In all cases there was some reduction in strength at the surface relative to the bulk ranging from a low of 2% to a high of 30%. The mill batches also showed variation in material properties with the differences in properties attributed to processing conditions. In order to understand the batch to batch variability an evaluation was completed which sought

possible correlation of strength with ten separate chemical and physical characteristics (variables) of 5 batches of powder (3 IPA milled, 2 water milled). Of the ten, only one (variable A) showed a significant correlation with strength, Figure 6. The process has been modified to consistently attain the lower levels of variable A.

Table 3: Average Strength (MPa)

Bed	Location	Batch S004	Batch S008	Batch S009	Location Average	Bed Average
1	Surface	709	691	750	717	768
	Bulk	893	800	766	819	
2	Surface	798	663	539	667	733
	Bulk	846	778	772	799	
Batch Average		812	733	707		750

Optimization of the gas-pressure sintering densification cycle has been completed. The best results to date for an aqueous processed sample are a mean flexural strength of 893 MPa and a fracture toughness of 7.4 MPa $\sqrt{m}$ (not shown). This optimized process will be used for the production of tensile components.

Figure 6: MOR Strength vs. Variable A Level

REFERENCES

"Development of Improved Processing and Evaluation Methods for High Reliability Structural Ceramics for Advanced Heat Engine Applications, Phase I", V.K. Pujari, et.al., Final

Report, ORNL/Sub/89-SB182/1, August 1993.

STATUS OF MILESTONES

All milestones on schedule. Milestone completed during reporting period:

- #1-2 (12/15/93) Demonstrate surfactants for > 48V% solids.
- #1-3 (12/15/93) Colloidal consolidation numerical model.
- #1-4 (1/31/94) Establish density gradient detection limits.
- #1-5 (3/31/94) Fabricate tensile bars from experimental suspension, establish green density gradient and mechanical properties after HIP'ing.
- #2-2 (12/15/93) Demonstrate stable castable GPS suspension.

PUBLICATIONS / PRESENTATIONS

"Closed Loop Colloidal Processing of High Reliability Silicon Nitride" by V.K. Pujari, et al was submitted 2/25/94 for Proceedings 1993 Automotive Technology Development CCM.

PROBLEMS ENCOUNTERED

None

Improved Processing

S. D. Nunn, O. O. Omatete, C. A. Walls, D. L. Barker, P. J. Jones,
and R. E. Simpson Oak Ridge National Laboratory

Objective/scope

The objective of the research is to determine and develop the reliability of selected advanced ceramic processing methods. This program is to be conducted on a scale that will permit the potential for manufacturing use of candidate processes to be evaluated. The emphasis is on silicon nitride. Issues of practicality; safety, hygiene, and environmental issues; and in-process testing methods are to be addressed in addition to technical feasibility. The methodology includes selection of candidate processes and evaluation of their range of applicability to various kinds of commercially available ceramic powders.

Technical highlights

I. Silicon Nitride Gelcasting

The gelcasting process repeatability study (milestone 114209) was completed ahead of schedule. Details of the study were reported in the previous semiannual. In summary: Eleven gelcasting batches were prepared with UBE E-10 silicon nitride powder containing 5 wt% Y_2O_3 and 5 wt% Al_2O_3 in a MAM/MBAM monomer solution. The dimensions of the dried green ceramic body and the dimensions, density, and modulus of rupture of the fired ceramics were measured. It was found that the overall variability of the samples was no greater than the variability within a given batch, indicating excellent repeatability from batch to batch.

II. Sintered reaction-bonded silicon nitride (SRBSN) Gelcasting

A series of compositions was prepared for evaluating the gelcasting of silicon metal for SRBSN. The slurries were prepared by adding the powders to a 15% solution of acrylic acid in water. The batch compositions are shown in Table 1. The molar ratio of $Si_3N_4:Al_2O_3:Re_2O_3$ was kept constant in the compositions. The gelcasting slurries contained 35 vol % powder. None of the compositions showed gas evolution during the mixing process, and all formed very fluid slurries which were easily deaired and cast. It was found that the slurries could be gelled either at room temperature or at elevated temperature (60°C). Gelling was completed in a shorter time (15 to 30 min) at the elevated temperature. The compositions containing yttrium and lanthanum appeared to form pores in the green body during the gelling process. The neodymium composition did not. Composition-dependent differences were also observed in the strength of the gelled bodies and dried green bodies. The samples containing yttrium were relatively soft and rubbery after gelling but dried to form extremely strong green bodies. The lanthanum and neodymium compositions were very rigid after gelling but dried to form weaker green bodies. Additional studies have indicated that the formation of pores during gelling is due to the decomposition of the rare-earth oxide at the gelling temperature (60°C). The porosity was eliminated when samples of yttria- and lanthana-containing slurries were aged for 1 h at 60°C or aged overnight at room temperature prior to the normal milling step. In addition, differences in the stiffness and strength of the gelled bodies, which had been noted previously, were no longer observed. When the yttria-containing slurry was aged, the gel exhibited similar characteristics to the neodymia and lanthana gels. The stiffness of the gelled body appears to be related to the degree of crosslinking in the polymerized gel. The highly crosslinked materials are very rigid, while a lower level of crosslinking produces a more rubber-like gel. The proper degree of crosslinking is required to achieve both a firm gelled body and a strong dried green body.

Two gelcasting slurries having the composition of sample 3 in Table 1 were prepared to produce samples for nitridation and sintering studies. One of the slurries had a solids content of 35 vol %, while the other contained 40 vol % solids. After gelcasting, drying, and binder burnout, samples

Table 1. Compositions for gelcasting of SRBSN

Sample	Composition, wt %					
	Si	Si ₃ N ₄	Al ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	Nd ₂ O ₃
As-prepared						
1	68.25	14.44	4.33	12.97		
2	64.54	13.66	4.10		17.70	
3	64.17	13.58	4.08			18.17
Reacted						
1		88.10	2.98	8.92		
2		84.75	2.87		12.38	
3		84.41	2.86			12.74

of the 35 vol % material were cold-isostatically pressed at different pressures to determine the effect of pressing on the green density and the subsequent nitridation and sintering of the samples. The results are shown in Table 2 and indicate that isopressing is desirable for increasing both the green and the fired density while having no noticeable effect on the excellent nitridation characteristics of the samples. The nitridation was conducted under flowing nitrogen at 25 psia with a peak temperature of 1450°C followed by furnace cooling. The sintering was done at 1800°C for 1 h with 30 psia static nitrogen pressure. Similar processing of a sample from the 40 vol % solids batch, isopressed at 55,000 psig, showed an apparent reduction in conversion of silicon-to-silicon nitride during the nitridation step but a much higher fired density of 98% theoretical. The nitridation step was varied from that used with the previous samples by including a 1-h hold at the 1450°C peak temperature. Additional tests will be required to explain the apparent differences in the processing results.

It had been found in earlier evaluations that the gels obtained from acrylic acid (AA) solutions containing dissolved lanthanum oxide were often brittle and crumbly. This was attributed to a high degree of crosslinking in the polymer gel. In an effort to increase the flexibility and toughness of the gel, a series of solutions was prepared consisting of different ratios of acrylic acid and methacrylic acid (MAA). The lanthanum oxide is less soluble in methacrylic acid, thus producing fewer crosslinking molecules. It was found that the solution containing 80% MAA and 20% AA formed an excellent gel. This system will be evaluated further to determine its compatibility with silicon metal.

A number of dispersing aids were evaluated for improving the dispersion of silicon metal powder in acidic solutions. The dispersing aids included: Darvan 811, Darvan 821A, Daxad 19, Daxad 19LCA, Dolapix 33, and Dolapix 75. Varying amounts of the dispersing aids were added to dilute (2 wt%) silicon suspensions. The sediment height was monitored and measured over a period of about 24 h. None of the dispersing aids tested was very effective in room-temperature tests. At slightly elevated temperatures (~40°C), the Dolapix 33 worked well. Further tests are planned when additional dispersing aids are received.

Table 2. A comparison of the effect of cold-isostatic pressing on the processing results of gelcast silicon metal containing neodymia as a sintering aid

Slurry solids %	Isostatic pressure (psig)	Green density (g/cm ₃)	Apparent silicon conversion*	Fired density† (g/cm ₃)	Theoretical density (%)
35	0	1.22	96.8‡	2.83	82
35	10,000	1.54	96.3‡	3.15	91
35	50,000	1.67	96.5‡	3.22	93
40	55,000		87.8**	3.38	98

*Calculation of the silicon conversion was based on the amount of silicon in the starting sample and the weight change after nitridation.

†Fired at 1850°C for 1 h under 30 psi nitrogen.

‡Nitridation to 1450°C, furnace cool.

**Nitridation to 1450°C, 1-h hold, furnace cool.

Our preliminary investigations have shown that the gelcasting process is a feasible method for forming components of SRBSN. Plans are now being made to expand the study of SRBSN gelcasting to include refinements of the gelcasting process, improvements in the SRBSN compositions, evaluation of the nitriding and sintering steps, and measurement of fired SRBSN properties.

III. Gelcast Green Body Properties

During the development of the gelcasting process for forming ceramic materials, it has been observed that the ceramic green bodies have unusual characteristics compared to conventionally processed materials. In particular, it was noted that the gelcast materials seemed to be exceptionally strong. A study was initiated to obtain a quantitative assessment of the green strength of gelcast ceramics. To compare the strength of green bodies prepared by different forming techniques, test samples of dry-pressed, slipcast, and gelcast materials were prepared. The samples were approximately 55 mm in diameter by 10 mm thick. The tensile strength of the samples was determined using a diametral compression test. In the test, a disk-shaped specimen is stood on edge, and a compressive load is applied along the vertical diameter of the sample. A tensile stress is generated normal to the applied load. For a brittle material, fracture will usually occur along the loading line due to the tensile stress. The magnitude of the tensile stress is given by:

$$\sigma = (2P)/(\pi Dt) ,$$

where P is the applied load, D is the diameter of the disk, and t is the thickness of the disk.

A summary of the test results is given in Table 3. Although the packing density of the green bodies varied from about 52 to 60%, there does not appear to be a direct correlation between the observed green density and the measured tensile strength. There is, however, a clear relationship between the forming method and the strength. The dry-pressed samples had the lowest strengths, 0.16 MPa (23 psi) for the samples with PVA binder only and 0.60 MPa (87 psi) for the samples containing PVA and Carbowax. The slipcast samples were considerably stronger, 1.88 MPa (273 psi). The gelcast samples showed the highest strengths, 2.93 MPa (425 psi) for the alumina containing 3 wt% binder and 3.24 MPa (470 psi) for the silicon nitride material containing 5 wt% binder.

The microstructure of the fracture surfaces of the test samples was examined using optical microscopy and scanning electron microscopy (SEM). There was a clear distinction between the roughness of the surfaces of the dry-pressed and slipcast samples compared to the gelcast material. The high degree of roughness of the dry-pressed and the slipcast samples indicated a nonuniform distribution of the binder and considerable particle agglomeration. There also appeared to be larger pores in the microstructure of these samples. In contrast, the gelcast samples showed a very uniform fracture surface indicating a homogeneous distribution of the binder in the microstructure. The gelation reaction forms a highly crosslinked acrylic polymer. When dried, this polymer is very strong, hard, and brittle. The uniform distribution of this binder in the gelcast materials, combined with the absence of large flaws due to particle agglomeration or porosity, appears to be the reason for the exceptionally high strength of these samples.

Table 3. Green body strength measured by diametral compression testing

Material*	Green body type	Binder (wt %)	Number of tests	Green density		Tensile strength (MPa)
				(g/cc)	% Th.D	
Alumina	Dry pressed	3.07% PVA	21	2.13	53.5	0.16 ± 0.03
Alumina	Dry pressed	3.75% PVA + 1.25% Carbowax	12	2.38	59.8	0.60 ± 0.20
Alumina	Slipcast	3.75% PVA + 1.25% Carbowax	6	2.11	53.0	1.88 ± 0.04
Alumina	Gelcast	3% MAM/MBAM	8	2.33	58.5	2.93 ± 0.85
Silicon Nitride	Gelcast	5% MAM/MBAM	7	1.68	52.1	3.24 ± 0.29

*Alumina: RC-HP DBM, Malakoff Industries, Malkoff, Texas; silicon nitride: SN E-10, UBE Industries, New York, New York.

IV. Non-Aqueous Gelcasting

Over the past several years, we have been concentrating on improving the properties and characteristics of water-based gelcasting systems. Some materials, however, are sensitive to moisture and must be processed in a non-aqueous environment. Aluminum nitride and certain high-temperature ceramic superconductors are good examples of such materials. We have begun to look at the possibility of gelcasting in an isopropyl alcohol-based system. Preliminary testing has been conducted on various combinations of our present "standard" gelcasting formulations (MAM/MBAM and MAM/PEG) and yielded disappointing results. Numerous trials

were conducted with alternative monomers, crosslinkers, and initiators, and two systems were found which yielded acceptable neat gels (no ceramic powder present). Both of these systems incorporate the monomer 1-Vinyl-2-pyrrolidinone (NVP) and the initiator 2,2'-Azobisisobutyronitrile (AIBN). Refinement of these gelcasting formulations and evaluation of their compatibility with various ceramic powders are now planned.

Status of milestones

Milestones 114209 and 114210 have been completed on schedule.

Publications and presentations

S. D. Nunn, "Gelcasting Technology," presented at the Ceramic Technology Quarterly Review Meeting, U.S. Department of Energy, Washington, D.C., December 16, 1993.

S. D. Nunn, O. O. Omatete, C. A. Walls, and D. L. Barker, "Tensile Strength of Dried Gelcast Green Bodies," presented at the 18th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, Florida, January 9-14, 1994.

1.2 CERAMIC COMPOSITES

1.2.2 Silicon Nitride Matrix

Optimization of Silicon Nitride Ceramics

K. J. Lee and T. Y. Tien (The University of Michigan)

Objective/Scope

To develop processing methods to optimize strength, toughness and creep resistance of monolithic silicon nitride ceramics. Silicon nitride ceramics with fiber-like β -Si₃N₄ grains will have higher fracture strength and toughness and better creep resistance. The fiber-like structure can be obtained by sintering the silicon nitride ceramics at high temperature under a nitrogen over-pressure. The mechanical properties can further be improved by controlling the size and the aspect ratio of the fiber like β -Si₃N₄ grains and the composition and nature of the grain boundary phase(s). The major goal of this project is to develop monolithic silicon nitride ceramics with optimum mechanical properties.

Technical Highlights

The α -Si₃N₄ to β -Si₃N₄ ratio (5% β -Si₃N₄) and impurity content are the same in all three powders. The particle sizes of E03, E05, and E10 are 0.95, 0.70 and 0.45 μ m, respectively. The additives used were Y₂O₃, Al₂O₃, MgO, and CaO, or combinations of these chemicals. The compositions studied were described by the sample designations. Two series of compositions were used. To study (1) effect of particle size on grain growth, the compositions contained 92 wt% Si₃N₄, 6 wt% Y₂O₃, and 2 wt% Al₂O₃. To study (2) effect of sintering additives, the samples ID 00, 02, and 20 contained the following: 90% Si₃N₄, 6% Y₂O₃ and 4% MgO for 00; 89.8% Si₃N₄, 6% Y₂O₃, 4% MgO and 0.2% CaO for 02; and 88% Si₃N₄, 6% Y₂O₃, 4% MgO and 2% CaO for 20.

Starting powders were weighed and attrition milled under isopropanol for 2 hours. Slurries were dried on a hot plate at 85°C under constant stirring to avoid segregation. Dried powders were isostatically pressed under a pressure of 14 MPa. Pressed pellets were sintered at different temperatures for a time period of 0.5, 1, 2 and 5 h under a static nitrogen pressure of 10 atmospheres in a graphite furnace. The specimens were placed in a BN crucible filled with BN powders.

The surfaces were ground, polished and etched with molten salts. The grains were then disintegrated using ultrasonic vibration. Loose grains were collected on a porous medium for microscopic examination.

Figure 1 shows three photomicrographs of disintegrated β -Si₃N₄ grains which illustrate the grain size differences between specimens using various starting silicon nitride powders. The length and width of these grains were measured and the results analyzed. A typical size distribution in both length and width direction are given in Figure 2. Normal distribution was observed for all sintered specimens. The mode from all of these size distribution measurements were used as the average grain size for further data treatments.

Specimens of different starting silicon nitride powders were sintered at 1800 and 1900°C for 0.5, 1, 2 and 5 h, and the results are given in Table 1. Table 2 gives the results of the effect on grain growth of specimens using different additives. The silicon nitride powders used for chemical effect studies were E10.

Figure 1. Micrographs of disintegrated β - Si_3N_4 grains. Specimens were E03, E05, and E10 sintered at 1900°C for 1 hr.

Figure 2. Size distributions of disintegrated β - Si_3N_4 grains. Specimens E03, E05, and E10 sintered at 1800°C for 1 h (a) grain length, (b) grain width.

Table 1. Measured average grain sizes and aspect ratios of β -Si₃N₄ ceramics sintered under 10 atm N₂.

Powder ID	Grain size	Sintering time (hr)			
		0.5	1	2	5
Ube E03	1800°C - L / W	5.25 / 0.615	5.85 / 0.813	8.90 / 1.00	8.85 / 1.908
	1900°C - L / W	7.55 / 1.415	8.90 / 1.84	10.02 / 1.96	10.5 / 2.33
	1800°C - AR	7.05	6.8	6.42	6.08
	1900°C - AR	5.70	4.94	4.65	4.55
Ube E05	1800°C - L / W	4.375 / 0.578	5.25 / 0.764	8.305 / 870	8.50 / 1.26
	1900°C - L / W	6.44 / 1.10	8.88 / 1.508	9.15 / 1.92	10.38 / 2.24
	1800°C - AR	7.3	6.9	6.5	6.4
	1900°C - AR	4.48	5.16	6.22	5.76
Ube E10	1800°C - L / W	3.82 / 0.496	4.45 / 0.60	5.22 / 0.715	5.75 / 0.75
	1900°C - L / W	4.38 / 0.798	6.70 / 0.988	7.55 / 1.00	9.23 / 1.215
	1800°C - AR	5.35	7.025	7.33	8.00
	1900°C - AR	4.80	5.75	6.02	6.18

Table 2. Measured average grain sizes and aspect ratios of β -Si₃N₄ ceramics sintered under 10 atm N₂ with different concentration of CaO addition.

Composition /		Sintering time (hr)		
Powder ID	Grain size	0.5	1	2
CaO 0% / 00	1800°C - L / W	2.102 / 0.563	2.470 / 0.590	2.775 / 0.810
	1900°C - L / W	2.302 / 0.675	2.711 / 0.712	3.075 / 0.990
	1800°C - AR	3.453	4.251	4.822
	1900°C - AR	3.733	4.551	4.725
CaO 0.2% / 02	1800°C - L / W	2.485 / 0.672	2.902 / 0.693	3.591 / 0.750
	1900°C - L / W	3.500 / 0.930	4.375 / 1.010	4.900 / 1.213
	1800°C - AR	4.280	4.801	5.652
	1900°C - AR	4.271	5.003	5.830
CaO 2.0% / 20	1800°C - L / W	2.450 / 0.672	2.622 / 0.690	4.153 / 0.783
	1900°C - L / W	2.625 / 0.813	3.974 / 0.870	5.501 / 0.931
	1800°C - AR	4.721	5.450	5.903
	1900°C - AR	4.102	4.522	4.851

The grain size data for specimens fired at 1800°C for different times were plotted in a log-log scale in Figure 3. These data fit the empirical equation, $D^n - D_0^n = Kt$. However, because of many uncertainties, we will not discuss the results in terms of this equation. Since the value of the exponent n indicates the growth mechanism, no attempt was made to assign a value to " n ".

(1) Effect of Particle Size

The size of β -Si₃N₄ grains in sintered specimens using E3 and E5 as starting materials grew larger in both length and width directions than those using E10 powder. This phenomenon can be explained using the relationship $K \propto D \gamma C_m$ where K is rate constant, D is diffusion coefficient, γ is interfacial energy and C_m is solute concentration. The above relationship applies to both diffusion-controlled and interface-limited growth processes. The smaller grains tend to have lower angle boundaries which results in a lower mobility, i.e., slower diffusion coefficient. Therefore, the specimen with larger particles grows faster.

(2) Effect of Sintering Additives

The above relationship can also be used to explain the effect of additives on the growth of β -Si₃N₄ grains. The eutectic temperature of a ternary system will be lower than that of a binary system, i.e., when one sintering additive is used, the melting temperature of the grain boundary phase is higher than when two additives are used. At the same temperature, the solubility of silicon nitride in the reactive liquid, C_m , is higher in the ternary system than in the binary liquid. The solubility is also higher in systems which are less refractory than in a liquid which is more refractory.

The solubility of Si₃N₄ in the systems studied in this investigation are not known. However, the solubility of SiO₂ in the Y₂O₃ and Al₂O₃ system is higher than in the Y₂O₃ and MgO system at the same temperatures. The grain growth results listed in Table 2 indicate that the β -Si₃N₄ grains grew larger when Y₂O₃ and Al₂O₃ were used as sintering aids than when Y₂O₃ and MgO were used. Use of CaO will also promote grain growth.

Status of Milestones

On schedule

Communications/Visit/Travel

None

Problems Encountered

None

Figure 3. Growth behavior of β - Si_3N_4 grains in ceramics sintered at 1800°C for different lengths of time. Compositions were E03, E05, and E10.

Reaction Sintering of α' + β' SiAlON Ceramics

K. Houser and T. Y. Tien (University of Michigan)

Objective/Scope

The objective of this project is to develop processing techniques to obtain silicon nitride ceramics with a controlled grain morphology for optimum mechanical properties at room temperature as well as at high temperatures. Silicon nitride ceramics exhibit high fracture strengths and high fracture toughness when the microstructure contains fiber-like β' -SiAlON grains. Obtaining these fiber-like β' -SiAlON grains depends upon the temperature, nitrogen pressure and the grains' interaction with other phases present. Ideally, if the equilibrium conditions between the phases present are understood as well as the kinetics controlling the growth of these fiber-like grains, one could ultimately tailor a silicon nitride ceramic's microstructure for certain mechanical properties. This project will focus on these structure-property relationships for a range of compositions in the Y,Si,Al/O,N system.

Technical Highlights

This project has worked with compositions from the α' + β' SiAlON region on the α' -SiAlON plane in the Y,Si,Al/O,N system. The α' plane is defined by the equation $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ and is illustrated in Figure 1. The β' phase is a substitutional solid solution where the (Si-N) is replaced by (Al-O). The α' phase is a stuffed derivative of the α -Si₃N₄ phase that incorporates some of the yttrium atoms into the unit cell as interstitials. The formation of these solid solutions reduces the amount of residual glass at the grain boundaries, which in turn allows for better high temperature mechanical properties.

Determination of the tie lines in the α' + β' region of the Y, Si,Al/O,N system has been one of the goals of this study in order to better understand the phase relationships within the system. Of the compositions that have been examined throughout the course of this research, the best densities and properties were achieved by compositions that boarder the two phase region. They were found to contain traces of a third phase, the 12H polytype of Si₃N₄ and therefore can not contribute to the study of tie lines in the two phase region. The study has made use of several compositions which do not densify by gas pressure sintering to determine these tie lines. These compositions are m=0.3, n=0.15; m=0.3, n=0.75; m=0.3, n=1.50; m=0.4, n=1.25; m=0.4, n=1.50; and m=0.5, n=1.25; and m=0.5, n=1.50 where m and n refer to the subscripts in the formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$.

One method of determining the tie lines is through use of the lever rule. Based upon the knowledge of both of the β' composition and percentage of phases present, the composition of the α' phase should be relatively simple to calculate. Several assumptions must be made, however, that could effect the accuracy of the calculations. One assumption is that the original composition has not shifted during sintering. Any shifts would most likely be attributed to the volatilization of SiO, and would be detectable through significant weight losses during sintering. Since the weight losses for these compositions were less than 1wt%, it has been assumed that the overall composition shift is negligible. This is being verified by microprobe and LPC techniques. Figure 2 represents the tie lines as determined so far.

Figure 1. Representation of the Y,Si,Al/O,N system: The α' -SiAlON plane.

Figure 2. Phase diagram for the α' plane in the Y,Si,Al/O,N system

The compositions which were found to gas pressure sinter to a density greater than 96% of the calculated theoretical density are summarized in Table 1 below. The various sintering schedules are also included. X-ray diffraction (XRD) showed that all samples consisted of the desired two phase α' + β' SiAlONs along with traces of the polytype 12H.

Compositions	Temperature, °C	Time
m=0.3, n=2.00	1940	2 hours
	1840	2 hours
	1740	2 hours
	1640	2 hours
	1640/1840	2 hours at each
m=0.4, n=1.75	1940	2 hours
	1840	2 hours
	1740	2 hours
	1640	2 hours
	1640/1840	2 hours at each
m=0.5, n=1.75	1940	2 hours
	1840	2 hours
	1740	2 hours
	1640	2 hours
	1640/1840	2 hours at each

Table 1. List of compositions and sintering schedules studied. The m and n represent the values in the formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$.

The fracture toughness and hardness of the various samples were determined by diamond indentation techniques and are shown in Figure 3 along with the varying densities of these samples. The fracture toughness follows the density trend, that is the highest densities result in the highest fracture toughness. The fracture toughness is also related to the grain size--at higher temperatures the β' grains are large and elongated and can increase the fracture toughness through crack deflection and bridging mechanisms. If the grain size gets too large, however, they may start to act as inclusions and not aid in toughening the material. The hardness is directly related to the amount of the phases present since the α' phase has a much higher hardness than the β' phase. As the α' content increases so does the hardness of the overall composition. The m=0.5 compositions have ~40vol% α' and demonstrate the highest hardness while m=0.4 compositions have ~30vol% α' and m=0.3 compositions have ~20vol% α' and show expected decreases in hardness.

Status of Milestones

On schedule.

Communications/Visits/Travel

None.

Problems Encountered

None.

Figure 3

Hot Pressed Si_3N_4 Ceramics

P. Vlahakis and T. Y. Tien (The University of Michigan)

Objective/Scope

The objective of this project is to investigate two-phase silicon nitride ceramics whose compositions lie on the $\alpha\text{-Si}_3\text{N}_4$ solid solution plane described by $\text{M}_m/3\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ in the Si,Al,M/N,O system. M represents metal cations and in this project the ions are supplied by the rare earth oxides Gd_2O_3 and Y_2O_3 . Compositions that lie on the Si_3N_4 - Rare Earth:9AlN join in this system have been studied. These materials, densified by a transient liquid phase during hot-pressing, showed very good mechanical properties at room temperature. However, the high temperature flexure strength exhibited a marked decrease after 1000 °C and it is thought that the presence of a glassy grain boundary phase is responsible. It is believed that additions of AlN in excess to that already in the compositions will reduce the amount of liquid produced during sintering. This should decrease or, preferably, eliminate the amorphous grain boundary phase and improve the high temperature properties. The effect of AlN additions on microstructural development and mechanical properties of hot-pressed Si_3N_4 ceramics will be investigated.

Background

The ceramics investigated in this study are two phase materials in the $\beta\text{-Si}_3\text{N}_4 + \alpha\text{-Si}_3\text{N}_4$ solid solution region of the $\alpha\text{-SiAlON}$ plane. The solid solution is formed by substitutions in the α -silicon nitride unit cell in which Al^{3+} ions replace Si^{4+} ions, O^{2-} replaces N^{3-} , and rare earth ions of 3+ valency are "stuffed" into interstitials to preserve charge neutrality. The solubility limits of each particular composition determine how many of the substitutions actually take place.

During densification the rare earth oxides and the oxides present as thin films on the Si_3N_4 and AlN particles (SiO_2 and Al_2O_3 , respectively) form a eutectic liquid. This liquid assists in particle rearrangement in the first stage of sintering. More liquid forms as the sintering temperature increases and wetting of AlN and Si_3N_4 causes the dissolution of these particles into the liquid. When the liquid reaches saturation $\beta\text{-Si}_3\text{N}_4$ grains precipitate out and this α - β transformation continues during, and is completed after, densification has occurred. These two mechanisms are competing processes and sufficient liquid must be present for both to occur. The solid solution formation also takes place during the presence of the liquid phase. The amount of each phase in the resulting microstructure is a function of the starting composition. For compositions in the $\alpha\text{-SiAlON}$ plane this is determined by the m and n values in the solid solution formula.

The morphology of the microstructure for this material typically shows high aspect ratio β grains. This tends to give good fracture toughness values due to the tendency of these grains to weave together in an interlocking pattern. The grains formed through the solid solution ($\alpha\text{-Si}_3\text{N}_4$ s.s.) tend to be small and equiaxed. These grains yield high hardness values. The resulting microstructure produces a ceramic that has excellent mechanical

properties.

Technical Highlights

For all the compositions in this study the values of $m=4$ and $n=2$ were used. Without additional amounts of AlN the compositions with these m,n values lie along the Si_3N_4 - Rare Earth:9AlN join. As the weight per cent AlN increases the compositions are pushed toward the nitrogen-rich corner of the Rare earth-Si-Al-O-N phase diagram. In practical terms this means that the amount of liquid present during sintering is reduced. It's been found that as the amount of liquid decreases, hot-pressing the powder compacts to full density becomes increasingly difficult. SEM micrographs of the compositions that did densify showed that the amount of residual liquid had apparently decreased, resulting in a smaller grain boundary phase. The micrographs also indicated that the expected morphology of elongated β grains and smaller, equiaxed grains did not develop. The volume of elongated β grains decreased with increasing additions of AlN. With 5 wt% AlN the microstructure showed no elongated grains, and a resulting fine-grained, equiaxed morphology.

Compositions containing Gd_2O_3 and Y_2O_3 were hot-pressed under flowing N_2 . A variety of heating rates, maximum temperature, and time at maximum temperature were used in an attempt to densify the compacts. Heating rates of 25-35 $^\circ\text{C}/\text{min}$ were used in combination with maximum temperatures in the range 1650-1800 $^\circ\text{C}$. Several hold times at maximum temperature were used. For compositions with small (<3 weight%) or no AlN additions hot press conditions of 25 $^\circ\text{C}/\text{min}$, 1700 $^\circ\text{C}$, and 1 hour at T_{max} resulted in fully dense samples. Density was measured by the Archimedes' method. X-ray diffraction patterns in all samples indicated the presence of both the solid solution and β - Si_3N_4 phases.

To date, bend specimens with Y_2O_3 sintering aid and aforementioned AlN additions have been prepared. The 52.2 mm x 26.2 mm billets were densified under flowing nitrogen at 1750 $^\circ\text{C}$ and 30MPa pressure for 1 hour in the hot press. Both sides of the billet were ground with progressively finer diamond grinding wheels to a thickness of 3 mm. Final grinding was performed with a 1000 grit wheel and a removal rate of 2 microns per pass. The low removal rate during final grinding was used to reduce the possibility of subsurface microcracking in the test specimens. The billets were cut with a diamond cutting blade at 2 microns per pass to a length of 48 mm, and in widths of 4 mm, with allowance given for material removal in the width direction. Final grinding in the width direction was also performed with a 1000 grit diamond wheel at 2 microns per pass. All grinding was performed in the direction of the long axis of the rectangle bar. The edges of the tension surface were chamfered at 45 $^\circ$ using a chamfering jig, to a depth of 80 microns, with a 1000 grit diamond wheel.

The tension surface of the bend specimen was polished with 15 micron diamond paste using a Buehler Automet Polisher. The wheel using in this operation is designed to remove material without introducing subsurface damage. After all grinding marks from the 1000 grit wheel were removed, the tension surface was polished by hand using 6 micron paste. Polishing was complete when investigation under the optical microscope at 50X showed no scratches. The chamfered surfaces were also polished to a 6 micron finish.

The results of room temperature 4 point bend tests are shown on the attached graph. The bars were tested on an Instron apparatus using a cross-head speed of 0.5 mm/min. The compositions containing 1 wt% and 0 wt% AlN additions showed strength levels more

typical for specimens of this size. Compositions containing 3 and 5 wt% additions has very low strength and have not been tested at elevated temperatures.

High temperature fracture strength as a function of AlN additions are shown. The 1 wt% specimens demonstrate higher fracture strength than the 0 wt% specimens and the difference is most pronounced at 800 °C. This may be attributed to the reduction of the amorphous grain boundary phase due to the AlN addition. This reduction in the glassy phase can be explained by the increase in the formation of α -SiAlON from the additional Al^{3+} ions. The reduction of the amount of liquid during sintering follows from the increase in solid solution formation. The precipitous drop in strength occurs after the softening point of the grain boundary glass is reached. The difference in slopes between the two compositions in this region of decreasing strength may be explained by the reduced volume of elongated β grains in the 1 wt% specimens. The interlocking of these high aspect ratio grains provides an additional strengthening mechanism, which is dominant once the softening point of the glass is reached.

1.2.3 Oxide Matrix

Dispersion-Toughened Ceramic Composite

T. N. Tiegs, S. D. Nunn, P. A. Menchhofer, D. L. Barker, and C. A. Walls
(Oak Ridge National Laboratory)

Objective/scope

Initially, this work involved development and characterization of SiC whisker-reinforced ceramic composites for improved mechanical performance. To date, most of the efforts involving SiC whisker-reinforced alumina, mullite, silicon nitride, and sialon have been completed. In addition, studies of whisker-growth processes were initiated to improve the mechanical properties of SiC whiskers by reducing their flaw sizes and, thereby, improving the mechanical properties of the composites. Currently, in situ acicular grain growth is being investigated to improve fracture toughness of silicon nitride materials.

Technical highlights

In situ Toughening of Silicon Nitride by Microstructure Development

Characterization of As-Fabricated Surfaces Formed During Gas Pressure Sintering (GPS) - During GPS at elevated temperatures, silicon nitride materials exhibit weight losses due to decomposition and loss of Si, N, and SiO. To minimize weight losses, samples are typically packed in powders that create a protective atmosphere. At temperatures $>1825^{\circ}\text{C}$, nitrogen gas over-pressures must also be used, in addition to packing powders, to suppress the decomposition of Si_3N_4 so that materials can be densified. Pressures of 1 to 10 MPa (10 to 100 atm) are usually required, and sintering additives are still needed.

The decomposition of the silicon nitride leads to a reaction layer at the surface of the parts. The thickness of the reaction zone can be quite variable with visible differences up to 2 mm from the surface common. For optimum mechanical properties, these reaction layers are machined off. It is well established that machining represents a major portion of the cost of silicon nitride parts, and efforts are under way to reduce its impact on the economics of these materials for engine applications. Consequently, it is desirable to minimize the reaction layers and thereby minimize the machining necessary. The ultimate goal would be to eliminate the reaction zone completely and use as-fabricated surfaces.

To examine the effects of processing on the formation of these reaction zones, a series of tests was performed. Important parameters affecting the reaction layers include the packing powder composition, crucible type, sintering temperature, nitrogen pressure, sintering time, use of barrier/protective coatings, and setter type. With this many variables, a Taguchi experimental array was formulated to assess the impact of each of the variables on a two-step GPS process (see Table 1). For each of the conditions listed in Table 1, three compositions of silicon nitride with different intergranular phases were tested. These compositions are Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 , Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ (at 5 equivalent % oxygen) and Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

The results from the GPS on weight loss, sintered density, and visible reaction layer thickness were reported previously.¹ The Si_3N_4 -6% Y_2O_3 -2% Al_2O_3

Table 1. Taguchi experimental design array for examination of reaction layers on the surface of silicon nitride ceramics. The design is an L_{18} ($6^1 \times 3^6$) with temperature, nitrogen pressure, time, and coating dummy-loaded to two variables.

Test No.	Packing powder ^a	Crucible material	Sintering temperature (°C/°C)	Nitrogen pressure (MPa)	Time (h/h)	Coating	Setter
1	Mixture	Graphite	1850/1900	0.3/0.6	2/1	No	BN
2	Mixture	BN	1900/1950	0.6/3.5	2/2	No	None
3	Mixture	RBSN	1900/1950	0.6/3.5	2/2	Yes	SiC
4	Low Ox.	Graphite	1850/1900	0.3/3.5	2/2	Yes	SiC
5	Low Ox.	BN	1900/1950	0.6/3.5	2/2	No	BN
6	Low Ox.	RBSN	1900/1950	0.6/1.0	2/1	No	None
7	Oxidized	Graphite	1900/1950	0.6/1.0	2/2	No	SiC
8	Oxidized	BN	1900/1950	0.6/3.5	2/1	Yes	BN
9	Oxidized	RBSN	1850/1900	0.3/3.5	2/2	No	None
10	BN	Graphite	1900/1950	0.6/3.5	2/2	No	BN
11	BN	BN	1850/1900	0.3/0.6	2/2	Yes	None
12	BN	RBSN	1900/1950	0.6/3.5	2/1	No	SiC
13	None	Graphite	1900/1950	0.6/3.5	2/1	Yes	None
14	None	BN	1900/1950	0.6/1.0	2/2	No	SiC
15	None	RBSN	1850/1900	0.3/3.5	2/2	No	BN
16	Mix ^b	Graphite	1900/1950	0.6/3.5	2/2	No	None
17	Mix ^b	BN	1850/1900	0.3/3.5	2/1	No	SiC
18	Mix ^b	RBSN	1900/1950	0.6/1.0	2/2	Yes	BN

^aMixture - Si_3N_4 -20% BN-5% Y_2O_3 ; Low Ox. - Si_3N_4 fired in nitrogen to 1800°C for 2 h; Oxidized - Si_3N_4 fired in air to 1000°C for 1 h; BN - 100% BN;

^bMix - Layer of Si_3N_4 -20% BN-5% Y_2O_3 on bottom of crucible (no contact with samples).

composition achieved high densities for all of the firing conditions used in the tests. On the other hand, the other two compositions with more refractory grain boundary phases showed quite variable densification. The $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition exhibited densities from ~88 to >100% T.D., and the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition had densities between 85 to 98% T. D. depending on the conditions. Because of the refractory nature of the sintering additives for these compositions, temperature was the most important factor affecting densification. In addition, at the lower initial sintering temperature of 1850°C, these compositions did not achieve closed porosity prior to the second high-temperature grain growth step. Consequently, for the tests where high gas pressure was used during the second step, further densification was inhibited by trapped gas. For the $\text{Si}_3\text{N}_4\text{-6% Y}_2\text{O}_3\text{-2% Al}_2\text{O}_3$ samples where closed porosity was achieved even at the lower initial temperature, high gas pressure applied during the second sintering step was effective to improve densification. The effect of packing powder on the densification for the various compositions is shown in Fig. 1. As indicated, only a small effect on densification of the $\text{Si}_3\text{N}_4\text{-6% Y}_2\text{O}_3\text{-2% Al}_2\text{O}_3$ samples was observed. However, the other two compositions showed a much stronger effect. For the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples, the highest densities were achieved with either BN or oxidized Si_3N_4 as packing powder. The $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ samples exhibited the best densification with BN or low-oxygen Si_3N_4 packing powder.

Observed weight changes occurring during sintering can be associated with numerous reactions as shown below:

Sample Decomposition:

Reaction (Sample and environment):

Reaction (Crucible or furnace heating elements):

High weight losses were associated with the use of graphite crucibles and indicate a reaction of CO or C with the samples and the formation of volatile species (see Fig. 2). The CO_2 formed, in turn, reacts with the available carbon, forming additional CO that can return to further decompose the sample. Oxygen depletion at exposed surfaces was also found in samples fired in non-graphite crucibles. Examination with an electron microprobe of a $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ sample sintered in a BN crucible showed an oxygen gradient across the surface reaction zone with the surfaces being deficient (see Fig. 3). This behavior indicates that the loss of SiO was occurring during sintering for essentially all samples at high temperature. X-ray analysis of the as-sintered surfaces of $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ samples (also sintered in BN crucibles) showed melilite ($\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$) present. None was observed in X-ray patterns from the interior regions, and this is further indication for SiO loss at the exposed sample surfaces. These phenomena suggest that the observed gradients are due, at least in part, to compositional changes

Fig. 1. Effect of packing powder on densification during GPS of silicon nitride for the different compositions.

Fig. 2. Observed mean weight losses during GPS of silicon nitride for the different crucible types and compositions.

Fig. 3. Oxygen concentration as a function of distance from the as-sintered surfaces of a GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 fired in a BN crucible.

across phase fields. This is illustrated in the Si_3N_4 -YN- SiO_2 - Y_2O_3 phase diagram (see Fig. 4), where loss of SiO drives the composition across three tie lines. At the Si_3N_4 -melilite tie line, decomposition of Si_3N_4 would drive the composition up to the right. Observed weight gains are attributable to nitrogen gas absorption into the intergranular liquid phase and to the possible formation of $\text{Si}_2\text{N}_2\text{O}$.

The optimum conditions for firing of the various compositions were determined based on either maximizing the sintered density, minimizing the visible reaction layer, or minimizing the weight loss. The results for each composition are shown in Tables 2 through 4. As indicated, the conditions for optimum density, reaction layer, or weight loss values are not necessarily the same. A set of parameters for firing to obtain the best overall combination of firing conditions is given in Table 5. To further determine the effects of the chemical and physical gradient on the mechanical properties, samples of the three compositions were prepared using the optimum conditions listed for Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$.

The change in flexural strength as a function of surface material removed is shown in Figs. 5 and 6. As shown, the strength of as-sintered surfaces of Si_3N_4 - Y_2O_3 - Al_2O_3 was reduced by more than 30% compared to the bulk material. The reduction in strength in the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples was not as dramatic at ~15%. In both cases, the bulk strengths were observed after removal of ≥ 0.5 mm of material from the as-sintered surfaces.

Microstructure Development During GPS - During GPS at elevated temperatures, silicon nitride materials exhibit elongated grain growth which leads to

Fig. 4. Silicon nitride corner of the $\text{Si}_3\text{N}_4\text{-YN-SiO}_2\text{-Y}_2\text{O}_3$ phase diagram showing how the loss of SiO from GPS samples can result in compositional changes across several phase fields.

Table 2. Optimized firing parameters for TRSN-44 gas-pressure sintered samples containing silicon nitride, alumina, and yttria

Firing parameter	Optimum condition for maximum density	Condition effect	Optimum condition for minimum reaction zone	Condition effect	Optimum condition for minimum weight loss	Condition effect
Packing Powder	Low Ox. or Mix ^a	Moderate	Mix ^a	Moderate	Mixture or Low Ox.	Moderate
Crucible Type	Graphite or RBSN	Moderate	BN	Very Weak	RBSN or BN	Weak
Temperature (°C)	1900/1950	Weak	1900/1950	Very Weak	1850/1900	Weak
Pressure (MPa)	0.6/3.4	Weak	0.6/3.4	Very Weak	0.3/3.4	Weak
Time (h)	2/2	Weak	2/1	Weak	2/2	Weak
Coating Presence	No	Weak	No	Weak	No	Weak
Setter Material	SiC	Weak	SiC	Weak	SiC or BN	Weak

^aMix - Layer of $\text{Si}_3\text{N}_4\text{-20% BN-5% Y}_2\text{O}_3$ on bottom of crucible (no contact with samples).

Table 3. Optimized firing parameters for TRSN-45 gas-pressure sintered samples containing silicon nitride, strontia, lanthana, silica, and ytterbia

Firing parameter	Optimum condition for maximum density	Condition effect	Optimum condition for minimum reaction zone	Condition effect	Optimum condition for minimum weight loss	Condition effect
Packing Powder	BN or Oxidized	Moderate	None or Oxidized	Strong	Oxidized or Low Ox.	Moderate
Crucible Type	Graphite or BN	Moderate	BN or RBSN	Moderate	RBSN or BN	Moderate
Temperature (°C)	1900/1950	Moderate	1900/1950	Weak	1850/1900	Weak
Pressure (MPa)	0.6/1.0	Moderate	0.6/1.0	Weak	0.3/3.4	Weak
Time (h)	2/2	Moderate	2/2	Weak	2/2	Weak
Coating Presence	Yes	Moderate	Yes	Weak	No	Moderate
Setter Material	BN or SiC	Weak	SiC or BN	Weak	BN or SiC	Weak

Table 4. Optimized firing parameters for TRSN-46 gas-pressure sintered samples containing silicon nitride, silica, and yttria

Firing parameter	Optimum condition for maximum density	Condition effect	Optimum condition for minimum reaction zone	Condition effect	Optimum condition for minimum weight loss	Condition effect
Packing Powder	BN or Low Ox.	Moderate	None or Oxidized	Moderate	Oxidized or Low Ox.	Strong
Crucible Type	Graphite	Moderate	RBSN or BN	Weak	RBSN or BN	Strong
Temperature (°C)	1900/1950	Strong	1850/1900	Weak	1850/1900	Moderate
Pressure (MPa)	0.6/1.0	Very Weak	0.3/0.6	Weak	0.3/3.4	Very Weak
Time (h)	2/2	Weak	2/1	Weak	2/2	Weak
Coating Presence	Yes	Moderate	No	Weak	No	Moderate
Setter Material	SiC or BN	Moderate	BN or None	Weak	SiC or BN	Weak

Table 5. Combined optimum firing conditions to maximize densification and minimize both reaction layer thickness and weight loss

Firing parameter	TRSN-44	TRSN-45	TRSN-46
Packing powder	Mix ^a	Oxidized	Low Ox.
Crucible type	RBSN	BN	BN
Temperature (°C)	1900/1950	1900/1950	1900/1950
Pressure (MPa)	0.6/3.4	0.6/1.0	1.6/1.0
Time (h)	2/2	2/2	2/2
Coating presence	No	No	No
Setter material	SiC	BN	BN

^aMix - Layer of Si₃N₄-20% BN-5% Y₂O₃ on bottom of crucible (no contact with samples).

Fig. 5. Flexural strength of GPS Si₃N₄-6% Y₂O₃-2% Al₂O₃ as a function of material removed from the as-sintered surface. Bulk sintered density was 98.8% T.D.

Fig. 6. Flexural strength of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ as a function of material removed from the as-sintered surface. Bulk sintered density was 100% T.D.

materials with high fracture toughness. A study was initiated to examine the effects of GPS processing parameters on the densification and mechanical properties of silicon nitride materials. Important parameters affecting the microstructural development include the sintering temperatures, sintering times, and heating rates. Because a number of variables were to be studied, a Taguchi experimental array was formulated to assess the impact of each of the variables on a two-step GPS process (see Table 6). For each of the conditions listed in Table 6, two compositions of silicon nitride with different intergranular phases were tested. These compositions are $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen). Fabrication of the test specimens is currently in progress.

Silicon Nitride Nanocomposites - Nanocomposites using matrices of alumina, magnesia, and silicon nitride have been reported to have improved strength and fracture toughness over the comparable monolithic materials.^{2,3} Most of the composite materials are based on a fine dispersion of SiC (<0.5 μm) particulates within the matrix. A limited study has been initiated to determine if any of these types of composites would be appropriate for GPS and attainment of high-toughness materials. The results from the preliminary study are summarized in Table 2. The SiC additions were made by using particles with <0.5 μm diam and using standard powder processing techniques. The matrix composition was $\text{Si}_3\text{N}_4\text{-4.6\% Y}_2\text{O}_3\text{-3.4\% Al}_2\text{O}_3$.

As shown, for these samples, the mechanical properties generally were lower for the composite materials. The particle size of the SiC addition was on the high side considered for nanocomposite-type materials. Because of the relatively large size, acicular grain growth of the $\beta\text{-Si}_3\text{N}_4$ grains was probably inhibited and resulted in the low fracture toughness values shown in Table 7. Additional samples will be

Table 6. Taguchi experimental design array for optimization of densification parameters to obtain silicon nitride ceramics with improved mechanical properties. The design is an $L_8 (4^1 \times 2^4)$

Test No.	Second sintering temperature (°C)	First sintering temperature (°C)	First sintering time (h) ^a	Second sintering time (h)	Heating rate to first sintering temperature (°C/min)
1	2000	1900	2 (min.)	2	50
2	2000	1950	2.5 (min + 1)	1	10
3	1950	1900	2 (min)	1	10
4	1950	1950	2.5 (min + 1)	2	50
5	1900	1900	3 (min + 1)	2	10
6	1900	1950	1.5 (min)	1	50
7	1850	1900	3 (min + 1)	1	50
8	1850	1950	1.5 (min)	2	10

^aMinimum time to obtain closed porosity (1900°C - 2 h, 1950°C - 1.5 h) with either no further hold time or a 1-h additional hold time. Times defined as minimum (min.) or minimum plus 1 h (min. + 1).

Table 7. Summary of densification and mechanical properties results on initial Si_3N_4 -SiC nanocomposites

Sample No.	SiC content (vol %)	Sintering conditions (°C/h/MPa)	Sintered density (% T.D)	Flexural strength (MPa)	Fracture toughness (MPa $\sqrt{\text{m}}$)
N0-T1	0	1900/2/0.3	98.5	806 ± 92	—
N0-T2	0	1850/2/0.4	99.3	—	6.8 ± 0.2
N0-T3	0	1850/2/0.4	99.6	705 ± 58	—
N1-T1	0	1850/2/0.4	99.6	847 ± 103	—
N2-T2	5	1850/2/0.4	99.5	—	6.5 ± 0.1
N2-T3	5	1850/2/0.4	99.9	823 ± 62	—
N3-T2	10	1850/2/0.4	99.5	—	6.1 ± 0.1
N4-T1	20	1900/2/0.3	96.0	631 ± 56	5.8 ± 0.2
N4-T2	20	1850/2/0.4	98.6	827 ± 34	5.6 ± 0.1

fabricated that will have a much finer SiC particle size ($<0.1 \mu\text{m}$) by using polymer precursors to determine if this is a significant factor.

Cooperative Research and Development Agreement (CRADA) [Materials and Electrochemical Research Corp.]

A CRADA has been established with Materials and Electrochemical Research Corp. (MER). ORNL is currently examining GPS of silicon nitride for densification and development of high-toughness materials using sintering aids designed to either form (1) rare-earth silicates or (2) rare-earth apatites as intergranular phases. MER is presently studying the effects on fracture toughness of (1) different starting $\alpha/\beta\text{-Si}_3\text{N}_4$ ratios and (2) additions of sintering aids as coatings (as compared to powders that are normally used).

Under the CRADA, materials made with different starting $\alpha/\beta\text{-Si}_3\text{N}_4$ ratios and with the addition of sintering aids as coatings instead of powders will be fabricated. The samples will be sintered by GPS using the optimum densification parameters developed for high-toughness materials in the ORNL program. Through the combination of efforts, silicon nitride ceramics with improved properties compared to current materials may result.

The development work is divided into four tasks as described below:

Task 1 - MER will fabricate samples with various starting $\alpha/\beta\text{-Si}_3\text{N}_4$ ratios. Most of the samples will be made with the sintering aids added as coatings. However, for direct comparison, at least one composition with the sintering aids added as powders will be made. Approximately four samples of six to eight different compositions will be fabricated under this task.

Task 2 - ORNL will fabricate samples with either rare-earth silicates or rare-earth apatites as intergranular phases and having various starting $\alpha/\beta\text{-Si}_3\text{N}_4$ ratios. The sintering aids will be added powders. Approximately four samples of six to eight different compositions will be fabricated under this task.

Task 3 - ORNL will GPS the samples using about four different conditions of time and temperature appropriate to obtain high-density parts.

Task 4 - Characterization of the samples will be split between ORNL and MER. ORNL will determine density of the sintered specimens, perform TEM of selected sintered specimens, measure fracture toughness by indentation/strength techniques, determine the flexural strength at temperatures between 1000 to 1400°C, and examine the creep resistance of selected samples. MER will determine density of the sintered specimens, perform TEM of selected coated Si_3N_4 powders, measure fracture toughness by single-edge notch beam techniques, determine the flexural strength at room temperature, examine selected samples by SEM, and perform X-ray diffraction on selected samples.

Status of milestones

On schedule.

Communications/visits/travel

Travel by T. N. Tiegs from October 21-22, 1993, to AlliedSignal Ceramic Components, in Torrance, California, to review their subcontract work involved with high-toughness silicon nitride.

Travel by T. N. Tiegs on October 7, 1993, to the East Tennessee Materials Research Society Meeting in Oak Ridge, Tennessee, to present a talk entitled "Processing and Properties of Silicon Nitride."

Travel by T. N. Tiegs on November 4-5, 1993, to the Southern Illinois University in Carbondale, Illinois, to review the subcontract work on continuous sintering of silicon nitride and present a talk to the graduate student seminar entitled "Processing and Properties of Silicon Nitride."

Travel by T. N. Tiegs from December 9-10, 1993, to the University of Michigan, in Ann Arbor, Michigan, to review their subcontract work involved with high-toughness silicon nitride.

Travel by T. N. Tiegs on January 9-14, 1994, to the American Ceramic Society Conference on Advanced Materials in Cocoa Beach, Florida, to present a talk entitled "Effect of Processing Parameters on Densification and Mechanical Properties of Gas-Pressure Sintered Silicon Nitride."

Travel by T. N. Tiegs from December 16-17, 1993, to MER Corp., in Tucson, Arizona, to discuss a CRADA on high-toughness silicon nitride.

Problems encountered

Problems with the temperature control on the GPS furnace have caused some delay in fabrication of the samples for the optimization of the processing parameters.

Publications

"Effect of Processing Parameters on Densification and Mechanical Properties of Gas-Pressure Sintered Silicon Nitride," by T. N. Tiegs, N. A. Gorey, S. D. Nunn, P. A. Menchhofer, D. L. Barker, and C. A. Walls, to be published in *Ceramic Engineering Science Proceedings*, American Ceramic Society, Westerville, Ohio.

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1.2.4 Low Expansion Materials

Characterization and Testing of Low-Expansion Ceramic Materials

D. P. Stinton and S. Subramaniam (Oak Ridge National Laboratory)

Objective/scope

Insulated exhaust port liners are needed in advanced diesel engines to increase engine fuel efficiencies by increasing the combustion temperatures and reducing the combustion heat that is lost through the head and into the water cooling system. Low-expansion materials have potential for this application because of their very low thermal conductivity, extraordinary thermal-shock resistance, and potential to reduce attachment stresses. Thermal shock resistance is critical because the shape of the port liners requires that they be cast into the metallic cylinder head. Because functioning exhaust port liners are inaccessible after being cast into cylinder heads, they must not require maintenance for the life of the head (~1 million miles). Contracts are being placed with Coors Ceramics Co. and Low Thermal Expansion Ceramics, Inc. (LoTEC) to develop cost-effective processes for the fabrication of port liners. Coors is investigating Al_2TiO_5 and $\text{Ca}_{1-x}\text{Mg}_x\text{Zr}_4\text{P}_6\text{O}_{24}$, while LoTEC is investigating $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ and $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$. A program has been initiated at ORNL to assist Coors and LoTEC with the characterization and evaluation of low-expansion materials.

Technical highlights

A systematic investigation of the mechanical and thermal properties of $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ (BaZPS) ceramics as a function of composition (Si at.%) and grain size is being carried out. Five compositions ($x = 0, 0.175, 0.250, 0.375$, and 0.500) were synthesized from stoichiometric proportions of the reagent-grade oxides using a solid state reaction method and sintered for 3000 min. To understand the influence of the grain size, three compositions ($x = 0, 0.174$ and 0.500) were additionally sintered for 30 and 300 min to result in smaller grain-sized samples. Room-temperature X-ray diffraction (XRD) results, high-temperature axial thermal expansion measurements of BaZPS with $x = 0.175$, room-temperature Young's modulus data, and high-temperature flexural strength results were reported earlier. In this report, the high-temperature XRD results of BaZPS with $x = 0$ are described. In addition, the effect of grain size on the bulk linear thermal expansion, Young's modulus, and flexural strength for BaZPS with $x = 0$ (BS0) is discussed.

High-temperature XRD was carried out to determine the axial thermal expansion of BaZPS with $x = 0$ using a Scintag diffractometer. XRD patterns were obtained in a helium atmosphere over the scan range of 9 to $140^\circ 2\theta$ at the rate of $0.1^\circ/\text{min}$ at $27, 300, 600, 900, 1000$, and 1250°C during heating, and at 800 and 27°C during cooling. Heating and cooling rates were $10^\circ\text{C}/\text{min}$, and the data collection was started after a 1-min hold at all the temperatures. Figure 1 shows the variation with temperature of the unit cell parameters "a" and "c" for BaZPS with $x = 0$. The unit-cell parameter "a" increased with increasing temperature until 1000°C and then decreased, while the "c" parameter decreased with increasing temperature until 900°C , and then increased with increasing temperature. The derivative of the unit-cell parameters plotted against temperature (see Fig. 2) revealed that there appears to be a phase transition occurring between 800 and 1000°C . Preliminary differential scanning calorimetry carried out on BaZPS with $x = 0$ showed that there is a reversible endothermic reaction occurring at 900°C . This coincides with the observation that two low-angle peaks disappeared above 900°C in the XRD

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Fig. 1. Variation of the unit cell parameters "a" and "c" with temperature. Note that the "a" parameter increases with increasing temperature (positive thermal expansion), and the "c" parameter decreases with increasing temperature (negative thermal expansion).

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Fig. 2 The derivative of the lattice parameter curves shown in Fig. 1 is plotted against temperature. Note the discontinuity at about 900°C that suggests a phase transition.

patterns. The results thus support the occurrence of a phase transition in BaZPS with $x = 0$ at 900°C.

The grain sizes of the BS0 compositions were determined by etching the polished surfaces with a 10% HF solution for 30 min. The density increased from 86.6 to 90.1 to 94.1% as the sintering time increased from 30 to 300 and finally 3000 min. As expected, the grain size increased from 1.8 to 2.7 to 5.0 μm as the sintering times increased from 30 to 3000 min. Specific results are summarized below.

Table 1. Correlation of grain size with sintering time

Sintering time (min)	Relative density (%)	Grain size (μm)
30	86.6	1.8
300	90.1	2.7
3000	94.1	5.0

The thermal expansion for BS0 was measured at heating and cooling rates of 3°C/min from room temperature to 1250°C using a Theta dual push-rod differential dilatometer. The thermal expansion curve for the BS0 compositions is shown in Fig. 3. It is interesting to note that the BS0 compositions expand only very slightly above 900°C, and the amount of expansion decreases with increasing sintering time. Also, the amount of hysteresis increases with increasing sintering time. The change in slope of the thermal expansion curve at 900°C confirms the phase transition identified by XRD.

Flexural strength and Young's modulus results are shown in Fig. 4, along with their standard deviations as a function of grain size. It is common wisdom that the mechanical properties increase with increasing density and increasing grain size provided that the grain size is below the critical grain size. In the present case, the properties are influenced by both density and grain size. However, both the flexural strength and Young's modulus decreased with increasing grain size (although there was increasing density) suggesting that the critical grain size for BS0 is less than 2.7 μm . The coefficient of bulk linear thermal expansion results also decreases with increasing sintering time, thus supporting our speculation. BS0 possesses high thermal expansion anisotropy and, hence, is expected to have a very low critical grain size.

Communications/visits/travel

D. P. Stinton and S. Subramaniam attended the Annual Contractors Coordination Meeting October 18-20, 1993, in Dearborn, Michigan. While in Detroit, representatives from Caterpillar, Cummins, Virginia Tech, Pennsylvania State University, ORNL, and DOE meet to discuss current work in the low-expansion ceramics program. The participants discussed characterization data reported by LoTEC and Golden Technologies (GTC). Mike Haselkorn of Caterpillar presented the results of finite element calculations of the casting process. His calculations indicated that a very low elastic modulus, in addition to

Fig. 3. Thermal expansion curves for BSO compositions sintered for various times. Note the change in slope at 900°C and that the hysteresis increases for increasing sintering times.

Fig. 4. Flexural strength and Young's modulus plotted as a function of their grain size. The decreasing strength and modulus imply that the critical grain size has been exceeded.

the low thermal expansion, will be required for port liners to survive the casting process. Mike's calculations, using an elastic modulus of 80 MPa, indicated that compressive stresses greater than 700 MPa were created during casting of both $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ and $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$. These stresses greatly exceed the compressive strength of the materials. Modification of the coefficient of thermal expansion to match that of cast iron failed to reduce the compressive stresses significantly. Successful casting of NZPs into cast iron will, apparently, require reduced elastic modulus or the use of compliant layers. Preliminary testing at Caterpillar indicates the $\text{Ca}_{1-x}\text{Mg}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ may have a lower elastic modulus than the other two NZPs.

The same calculations made with GTC's Al_2TiO_5 , with an elastic modulus of only 20 MPa, showed compressive stresses of only 200 MPa, which is much more reasonable for these relatively weak materials. Tom Yonushonis, of Cummins, reported that Al_2TiO_5 port liners had been successfully cast into cast-iron heads in a recent trial at Cummins. These port liners, however, did have a compliant layer added to the exterior surface to reduce the compressive stresses.

D. P. Stinton, Dinesh Agrawal, Deidre Hirschfeld, and Santosh Limage visited Detroit Diesel Corporation (DDC) on November 5, 1993, to discuss the use of ceramic port liners in DDC engines. Nabil Hakim and Tony Kaushal have been interested in compliant layers for some time and feel that compliant layers will be required to successfully cast any of the ceramic materials into cast-iron heads.

D. P. Stinton attended a program review at Corning on November 30, 1993, to discuss their program to extrude large regenerators from various low-expansion materials that included $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$.

Publications

A paper entitled "Synthesis and Cell Refinement of $\text{Ba}_{0.5+x/2}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ with $x = 0$ and 0.175" was accepted for publication in *Powder Diffraction*.

Development of NZP Ceramic-Based "Cast-in-Place" Diesel Engine Port Liners

Santosh Y. Limaye, (LoTEC, Inc.)

Objective/Scope

The overall objective of this research program is to develop sodium-zirconium-phosphate (NZP) ceramic based "cast-in-place" diesel engine port liners. Specific objectives are: (1) Materials requirement analysis, (2) successful demonstration of metal casting around the ceramic, (3) Cost-effective process development, and (4) Develop high temperature database (stability, thermal cycling, thermal shock).

Technical Progress

Metal Casting Trials

One of the primary goals of this project is the demonstration of the ability to cast molten metal around a (NZP) type ceramic shape without causing damage to either the ceramic or the solidified metal casting. Three metal casting trials were successfully completed this period, demonstrating the ability to cast the ceramic in place. Finite element analysis determined that in order for the ceramic to survive the casting-in-place, the ceramic would need to have either a lower elastic modulus (higher strain to failure) or a compliant layer to absorb the stresses associated with the thermal expansion mismatch between the ceramic and solidified metal. The compliant layer approach was tested. Two ceramic compositions and two ceramic shapes were chosen for the metal casting trials. The compositions chosen for these trials were BS25 ($\text{Ba}_{1.25}\text{Zr}_4\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24}$) and CS50 ($\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$). These compositions have ultra-low and low coefficients of thermal expansion (CTE) respectively and very low thermal expansion anisotropy. The average CTE of BS25, room temperature to 1000°C , is $0.7 \times 10^{-6}/^\circ\text{C}$ and for CS50 over this range the CTE is $1.9 \times 10^{-6}/^\circ\text{C}$. The ceramic test shapes were tubes with an outside diameter of approximately 50 mm, with a 5 mm wall thickness. The tubes were either straight or a 90° elbow. The tubes were covered with a porous ceramic compliant layer. Visual inspection of the cast metal/ceramic parts did not reveal any damage to either the metal or ceramic. A crude test was performed to determine the impact resistance of the ceramic with in the metal casting. The metal/ceramic was dropped repeatedly from approximately 2 meters on to a concrete block. The ceramic tube was checked for cracks, chipping, and any loosening from the surrounding metal. There was no apparent damage to the ceramic.

X-ray computer tomography was performed to examine the interface of the metal and ceramic compliant layer. It was found that at any point where there was direct contact between the metal and the ceramic tube (a void in the compliant layer) a small crack in the ceramic would develop. The cracks are approximately 0.05 to 0.1 mm wide and would extend up to 5 mm in length from the contact point. Future work will include the optimization of the compliant layer (thickness, porosity and compressibility) and the application process.

Process Development

During this period efforts have been on going to develop new binder and dispersant systems to help optimize the slip casting process. During the previous period, process development centered on powder calcination variables and milling procedures. It was determined that the current binder/dispersant system used for BS25 did not perform well when applied to CS50. Additionally the current binder tends to migrate during the drying stage of the slip casting process. New binders and dispersants are being evaluated to better optimize the formation of net shaped ceramic port liners.

Another shape forming process, pressure slip casting, is being investigated. Continued work is being done to optimize various casting parameters (pressure, time, slip viscosity, mold preparation) to produce cast parts at a higher casting rate with better dimensional tolerances.

Materials Characterization

A series of BSX ($\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_2\text{O}_{24}$) and CSX ($\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$) samples were subjected to heating and cooling cycles from room temperature to 1250°C. Compositions from the BSX series exhibit varying degrees of anisotropy and bulk linear thermal expansion as a function of concentration of silicon. Figure 1 shows the effect of composition on thermal expansion anisotropy. As expected compositions with a high degree of anisotropy exhibit large thermal expansion hysteresis (due to microcracking) and compositions with little anisotropy have relatively negligible hysteresis.

The stability of this ceramic material, when subjected to thermal cycling is being determined. During this period the effect of 1, 25 and 250 thermal cycles to 1250°C on the

Figure 1: The thermal expansion anisotropy and the axial expansion of BSX as a function of composition (silicone content)

bulk linear thermal expansion of the BSX series and CSX series was completed. For the BSX series $x=0.0, 0.17, 0.25, 0.375$ and 0.5 and for the CSX series $x=0.25, 0.375$ and 0.5 .

The generally isotropic compositions (BS17, BS25 and CS50) have little or no micro cracking associated with cooling from either the sintering temperature or the cyclic temperature. Without micro cracking there is very little thermal hysteresis and thus very reproducible thermal expansion curves. This is especially true for BS25 and CS50, the compositions chosen for the metal casting trials. Figure 4 and 9 show that there is little difference between the heating and cooling portion of the thermal expansion curve, even after repeated cycling to 1250°C .

All of the anisotropic compositions in these series (BS0, BS37.5, BS50, CS25 and CS37.5) had some initial shrinkage associated with the first thermal cycle, but then remained nearly constant. These compositions also have the largest degree of thermal hysteresis (due to micro cracking) and the greatest variation in bulk linear thermal expansion after thermal cycling. Although the anisotropic compositions have less reproducible thermal expansion curves, they consistent and reproducible. Future work will try to determine some of the factors affecting the bulk linear thermal expansion and thermal hysteresis of the anisotropic compositions. Figures 2 through 9 show the bulk linear thermal expansion curves for each of the compositions tested at intervals from as sintered to 1 cycle, 25 cycles and 250 cycles to 1250°C .

High Temperature Testing

High temperature elastic modulus measurements: The elastic modulus of BS25 was measured from room temperature to 1325°C using an ultrasonic measurement technique. A bar shaped sample was suspended in a furnace from two sapphire threads acting as ultrasonic wave guides which were connected to two transducers, one acting as a source and the other as a receiver. The temperature was raised slowly to 1325°C . The elastic modulus was measured at every 100°C intervals. Figure 10 shows the results of the measurements. This work was performed at Pennsylvania State University.

Figure 2: Effect of thermal cycling on the bulk linear thermal expansion of BS-0

Thermal Expansion **BS-17 Sample #1**

T. Barrett Jackson, LoTEC, Inc.
ORNL-HTML Industrial Fellowship Program

Figure 3: Effect of thermal cycling on the bulk linear thermal expansion of BS-17

Figure 4: Effect of thermal cycling on the bulk linear thermal expansion of BS-25

Thermal Expansion

BS-37.5 Sample #3

T. Barrett Jackson, LoTEC, Inc.
ORNL-HTML Industrial Fellowship Program

Figure 5: Effect of thermal cycling on the bulk linear thermal expansion of BS-37.5

Figure 6: Effect of thermal cycling on the bulk linear thermal expansion of BS-50

Figure7: Effect of thermal cycling on the bulk linear thermal expansion of CS-25

Figure 8: Effect of thermal cycling on the bulk linear thermal expansion of CS-37.7

Figure 9: Effect of thermal cycling on the bulk linear thermal expansion of CS-50

Figure 10: Elastic modulus of BS25 as a function of temperature. There is little change up to 1000°C.

Status of milestones

Program on schedule

Communications/Visits/Travel

1. T.B. Jackson, S.Y. Limaye, and W.D. Porter, "Effect of Thermal Cycling on the Physical and Mechanical Properties of [NZP] Ceramics," to be presented at the 96th Meeting of the American Ceramic Society, Indianapolis, IN, April 24-28, 1994.

Problems Encountered

None.

Publications

Following papers are being prepared for publication:

"Microcracking in the system $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ by Acoustic Emission Method"

"Thermal Expansion of [NZP], $\text{NaZr}_2\text{P}_3\text{O}_{12}$ -Type Materials"

References

None.

**Development of Low Thermal Expansion Ceramic-Based
"Cast-in-Place" Diesel Port Liners**

D. Coors (Golden Technologies Company, Inc.)

Objective/scope:

The objective of this work is to develop a low thermal conducting high thermal shock resistant ceramic port liner which will survive casting in gray iron and diesel engine operation.

Technical progress

To achieve the program objective, three key tasks have been defined:

- TASK 1: Fabrication of Test Specimens -- The goal in this task is to develop a material properties database for modeling port liner performance in casting as well as engine operation. This database will also serve as a reference point for improving necessary material parameters.
- TASK 2: Materials Requirements Analysis -- The purpose of this task is to develop a finite element model to analyze emperature distributions and associated thermal stresses in ceramic lined metal parts. This finite element model was created to simulate the casting of metal around exhaust ports of Aluminum Titanate, CMZP, and NZP materials.
- TASK 3: Process Development -- This task focuses on the processing of port liners, specifically process control variables such as milling, casting, drying, and firing. This also includes alternative methods of fabrication such as pressure casting

Technical progress towards achieving these tasks during this semi-annual period is described below.

Fabrication of Test Specimens

Two inch diameter tubes of Aluminum Titanate (AT-80) were fabricated by conventional slip casting methods. These tubes were then cut into test specimens with the dimensions 3mm X 4mm X 50mm. The specimens were tested using standard methods for the following properties: Green Bulk Density, Fired Bulk Density, Thermal

Expansion, Thermal Conductivity, Flexural Strength, Thermal Shock Resistance and Micro-cracking. The results are shown in the following table and curve:

Property	Units	AT-80				
		Room Temp.	100°C	400°C	700°C	1000°C
Density	g/cc	3.1				
Flexural Strength (MOR)	MPa	28	29	33	37	40
Elastic Modulus	GPa	4.3	5.5	10	15	19
Thermal Conductivity	W/m°K	1.1	1.2	1.5	1.9	2.2
Specific Heat	$\frac{J}{kg^{\circ}K}$	0.23	0.23	0.25	0.27	0.29
Thermal Shock Resistance ΔT	°C	1000				

FIGURE 1: Material Properties Comparison

AT-80 Thermal Expansion Curve

FIGURE 2: Thermal Expansion Curve for Aluminum Titanate

Micro-cracking Studies:

The following describes highlights from initial micro-cracking studies conducted at Penn State University by D.K. Agrawal and Else Breval. Test specimens from baseline material (Sample A: Figure 3), and baseline material after thermal upshock to 1500°C (Sample B: Figure 4) were prepared for acoustic emission characterization. The test results show a clear distinction between the two samples. Sample A had a main peak of acoustic emission at approximately 200°C, whereas Sample B had a main peak at 325°C with a higher level of acoustic activity..¹ Agrawal and Breval recommended examining additional samples from various experimental conditions in order to optimize the processing of AT-80.

Materials requirements analysis

Materials requirements analysis involved finite element studies of the metal casting process to determine the material properties necessary for successful casting of gray iron around ceramic tubes. AT-80 and various NZP compositions were physically tested as well as modeled using finite element codes. Stresses resulting from the cooling and shrinking of the metal were calculated and confirmed by other models. This work was subcontracted to Rogers and Associates in Salt Lake City, Utah and carried out in cooperation with GTC and LoTEC, Inc. of Salt Lake City, Utah. The final report for this task is being written.

Process development

Three 3 kilogram test batches of AT-80 were formulated and baseline slip was repeated using the smaller scale formula (3kg vs. 90kg). Milling time for the test batches was reduced from twenty four hours to nine hours by milling in two separate stages. The dispersant level was thought to be high because of mold discoloration over long periods of time. A batch was made reducing the dispersant amount by 60% and there were no noticeable differences between this batch and the others during the material slop casting and firing.

Data was also gathered concerning the mold life of plaster molds. The average mold life depended on the complexity of the molds. The number of parting lines seemed to have the most effect on deterioration. Molds with three parting lines lasted 7 to 10 castings before mold wear and casting rates increased noticeably. The casting rate would increase about 25% after the 7-10 castings were made. More importantly, the wear caused by repeated assembly and disassembly and from cleaning made casting increasingly difficult and shape changes in parts were observed. Two piece molds lasted longer; 10 to 13 casts, before they had similar results from wear. One piece tube molds exhibited a slight increase in casting time after 10 casts, however, wear was not a problem even after months of casting.

Casting rates were studied using three separate molds and two different batches of slip. The casting rate remained relatively constant between the molds and batches of slip. The temperature and humidity were held as constant as possible for all three test runs. Sets 1 and 2 are baseline material and set 3 is a small test batch. The results show that data points relate to a curve proportional to the square root of time.

FIGURE 5: Casting Rate Curve for Aluminum Titanate

Firing studies were carried out to examine the effects of temperature, and ramp rate on slumping, fired bulk density, and thermal expansion properties. Density increased with temperature and decreased as the ramp rate was increased. This was as expected. The slumping was also measured. Two inch O.D. tubes for measurement comparison at 0 and 90 degree axes were settered with the 0 degree axis horizontal to the setter plate. The tubes were placed on a small mound of setter sand so that the open ends were not in contact with the setter sand or plate. This method was intended to induce the maximum slumping with minimum setter drag. The firing profiles varied from a ramp rate of 100°C/hr to 200°C/hr and soak temperatures were between 1380°C and 1550°C. Slump increased with temperature and soak time as did the density. Because the slump was heavily influenced by wall thickness the data could not be easily quantitatively analyzed. Slumping occurred even at temperatures near the temperature of the formation of Aluminum Titanate (~1380°C) therefore, it was concluded that slumping could not be avoided, rather, it must be controlled. In an additional firing, 30 tubes with thicknesses varying from 0.100 - 0.215 were settered in the same manner and slumping versus wall thickness could be determined for a particular firing cycle. The results show the ratio of the fired 0 and 90 degree axes vs. the green tube ratio for varying wall thicknesses. Data relating thermal expansion behavior to these firing conditions is being collected.

FIGURE 6: Slumping Analysis Results

Status of Milestones

• Disseminate data to program participants	Behind Schedule
• Disseminate modified material data	Behind Schedule
• Disseminate trial casting data	On Schedule
• Program Management	On Schedule

Publications

None

References

- 1 D.K Agrawal and E. Breval, Pennsylvania State University, "Study of Microcracking Phenomenom of Aluminum Titanate and CMZP Ceramics by Acoustic Emission Method", unpublished report submitted to Golden Technologies, Feb. 1994.

1.3 THERMAL AND WEAR COATINGS

Fabrication and Testing of Corrosion-Resistant Coatings

W. Y. Lee, Y.W. Bae, and D. P. Stinton (Oak Ridge National Laboratory)

Objective/scope

Sodium corrosion of SiC and Si₃N₄ components in gas turbine engines is a potentially serious problem. The outer surfaces of SiC and Si₃N₄ parts oxidize at high temperatures to form an SiO₂ layer which inhibits further oxidation. However, sodium which is present in high-temperature combustion atmospheres reacts with the SiO₂ layer, such that it is no longer protective. The objective of this program is to develop a coating that will protect the underlying SiC or Si₃N₄ from sodium corrosion and provide simultaneous oxidation protection. To evaluate the behavior of potential materials such as stabilized ZrO₂ or HfO₂, TiO₂, Al₂O₃•TiO₂, and Ta₂O₅ in sodium-containing atmospheres, the corrosion resistance of hot-pressed samples of these materials will first be evaluated. A chemical vapor deposition (CVD) process will be developed for the application of the most promising coatings. The effect of the combustion environment upon coating characteristics such as microstructure, strength, adherence, and other properties will then be evaluated.

Technical progress

As discussed in the previous semiannual report, the Ta₂O₅-CVD process has been tailored to produce a well-coalesced, void-free coating microstructure. In summary, the use of the CO₂ + H₂ mixture as a source of oxygen for the deposition process was found to be effective in promoting the growth of the void-free microstructure. The coating was characterized to be highly crystalline, textured orthorhombic b-Ta₂O₅ by X-ray diffraction (XRD). The Ta₂O₅ grains were preferentially oriented to the [001] direction. The growth rate of Ta₂O₅ generally increased with temperature with an apparent activation energy of 228 kJ/mole. In general, the coating consisted of 1 to 3 μm size grains which appeared to be relatively well coalesced during their growth. The presence of voids (larger than the detection limit of scanning electron microscopy) in the coating microstructure was not observed. However, it was observed that very fine microcracks began to appear on the Ta₂O₅ coating surface, as the Ta₂O₅ grains became coalesced.

In this reporting period, the stability of the Ta₂O₅+Si₃N₄ system in oxidative and corrosive environments was tested. Also, samples for burner rig testing at AlliedSignal Engines were prepared.

(1) Oxidation and Corrosion Results

(a) Experimental Procedure

Hot-isostatically pressed Si₃N₄ substrates (GN10, AlliedSignal; 1 x 0.4 x 0.3 cm) were coated with CVD Ta₂O₅. Figure 1 shows that the coating was well adhered to the Si₃N₄ substrate and was uniformly deposited. The average

Fig. 1. Backscattered cross-section image and elemental X-ray maps of as-deposited Ta_2O_5 CVD coating.

thickness of the coating was typically in the range of 2 to 10 μm . The coating was identified to be textured orthorhombic b-Ta₂O₅ by XRD. Note that the apparent appearance of some Si in the as-deposited layer (see Fig. 1) was a spectral artifact. More detailed wavelength dispersive spectroscopy (WDS) and Auger electron spectroscopy analyses revealed that the coating did not contain any Si.

In corrosion experiments, a liquid dropper was used to dispense a saturated solution of Na₂SO₄ while heating the coated as well as some uncoated samples to 200°C using a hot plate. The specimens were typically loaded with 15 to 35 mg/cm² of Na₂SO₄. This loading level was higher than that used by Jacobson and Fox (1 to 5 mg/cm²) [see 1]. Jacobson and Fox observed that the general corrosion behavior of Si₃N₄ was not significantly influenced with increasing the Na₂SO₄ loading from 1 to 5 mg/cm². They also measured that the rate of Na₂SO₄ evaporation, in the absence of corrosion reactions, was about 0.016 mg/cm²/h at 1000°C and 101 kPa. Thus, the premature loss of Na₂SO₄ due to evaporation was not expected during the present corrosion experiments conducted for the duration of 5 to 100 h at 1000°C and 101 kPa. The Na₂SO₄ loaded specimens were placed on an Al₂O₃ holder and exposed to a flowing oxygen environment in a quartz tube heated using an electrical resistance furnace. The flow rate of oxygen was 200 cm³/min at STP and was controlled using a mass flow meter. The temperature was measured and constantly monitored using an optical pyrometer.

The corroded specimens were mounted in epoxy and polished using kerosene as a lubricant to examine corrosion products and resulting surface microstructures. Some specimens were washed in warm, distilled water before mounting to ascertain the effect of washing. A JEOL Superprobe 733 electron microprobe analyzer (EMPA), a Hitachi S-800 field emission scanning electron microscope (SEM), and a Scintag V X-ray diffractometer were used for microstructure characterization and phase identification.

(b) Oxidation

In Figs. 2(a) and (b), the XRD patterns of the Ta₂O₅-coated Si₃N₄ sample before and after exposure to flowing O₂ at 1000°C and 101 kPa for 100 h are shown. The as-deposited coating was crystalline and preferentially oriented to the [001] direction. Since Ta₂O₅ is a dense material, X-ray reflections from the underlying Si₃N₄ were very weak, although the coating was relatively thin. In comparison of the two patterns, it appeared that the crystal structure and the preferred orientation of the coating were not influenced by the oxidation treatment at 1000°C. The SEM analysis also indicated that the surface morphology of the coating was not affected much by the treatment.

The oxidation treatment at 1300°C in air for 50 h did not cause significant changes in the XRD pattern of the coating [see Fig. 2(c)] except for the appearance of some new, but very weak peaks. After 50 h in air at 1400°C, the intensity of the new reflections became stronger and dominant as shown in Fig. 2(d). The EMPA analysis showed that the coating still contained Ta and O as major elements. However, based on existing JCPDS files,² the origin of the new diffraction peaks could not appropriately be identified.

Fig. 2. XRD patterns of Ta_2O_5 -coated Si_3N_4 : (a) as-deposited, (b) after 100 h in O_2 at 1000°C , (c) after 50 h in air at 1300°C , and (d) after 50 h in air at 1400°C . Note that a minor peak at $\sim 21^\circ$ and a smaller shoulder around 23° in (a) were from a wax material which was used to mount the sample in the diffractometer.

Visually, the surface appearance of the coating treated at 1400°C became somewhat glassy. At a microscopic level, the surface morphology of the coating after the 1400°C treatment appeared somewhat similar to that of the as-deposited Ta₂O₅ coating, except for the presence of very fine, layered-like surface features. The coating was still adhered to the substrate after the treatment. However, some portion of the coating spalled off during polishing. The weight gain of the samples following the 1000 and 1300°C treatments was very small, 0.2 and 0.4 mg, respectively. This compared favorably to the fact that an uncoated Si₃N₄ sample gained 0.3 mg after 100 h at 1000°C in O₂. On the other hand, the sample which underwent the 1400°C treatment lost 3.3 mg. These results, along with the morphological changes observed from the XRD analysis, suggested that the Ta₂O₅-Si₃N₄ system became relatively unstable above 1300°C.

(c) Corrosion of Uncoated Si₃N₄

The XRD patterns of an uncoated Si₃N₄ sample following various treatment steps are shown in Fig. 3. After oxidation at 1000°C in O₂ for 100 h, the diffraction pattern was basically unchanged [Figs. 3(a) and 3(b)]. Also, after exposure in the Na₂SO₄+O₂ environment at 1000°C for 100 h, the pattern was not significantly changed except for the appearance of a new diffraction peak around 22° which was attributed to the formation of cristobalite [Fig. 3(d)]. Figure 3(c) shows the XRD pattern of the sample after loading Na₂SO₄ but prior to the corrosion treatment. The absence of any diffraction peaks attributable to Na₂SO₄ in Fig. 3(d) suggested that all Na₂SO₄ was consumed during the corrosion treatment.

Figure 4 shows a polished cross-section image and elemental X-ray maps of the corroded Si₃N₄ sample. The sample was attacked by corrosion to a depth of ~20 µm. The presence of Na, Si, O, and Y was observed in this region, but no sulfur was present (at least within the sensitivity of EMPA). The segregation of Y in the upper region was observed, leaving a Y-depleted zone of ~10 µm. The yttrium enrichment near the surface was also evident from the backscattered electron image. These results were consistent with the observations previously made by Jacobson and Fox.¹ They exposed an Si₃N₄ sample containing Y₂O₃ and Al₂O₃ binders to Na₂SO₄/O₂ at 1000°C for 147 h and observed that about 35 µm of the Si₃N₄ structure was attacked by corrosion. An ~15-µm Y-depleted region was observed due to the segregation of yttrium near the surface, and no sulfur was detected in the corrosion-affected zone.

(d) Corrosion of Ta₂O₅ coated Si₃N₄

Figure 5 shows a cross-section image and elemental X-ray maps of the Ta₂O₅-coated sample after exposure in the Na₂SO₄+O₂ environment for 5 h but prior to washing. It was clearly evident that, even within 5 h, the Ta₂O₅ coating layer reacted substantially with Na₂SO₄ as indicated by the presence of Na in the layer. As shown in the micrograph, the reacted layer became detached from the substrate during polishing. As discussed earlier, the appearance of Si in the reacted layer was determined to be a spectral artifact. The XRD analysis [Figs. 6(a)

Fig. 3. XRD patterns of Si_3N_4 : (a) as-received, (b) after oxidation in O_2 at 1000°C for 100 h, (c) after loading Na_2SO_4 , and (d) after corrosion in $\text{Na}_2\text{SO}_4 + \text{O}_2$ at 1000°C for 100 h.

Fig. 4. Backscattered cross-section image and elemental X-ray maps of Si_3N_4 after corrosion in $\text{Na}_2\text{SO}_4 + \text{O}_2$ at 1000°C for 100 h.

Fig. 5. Backscattered cross-section image and elemental X-ray maps of Ta_2O_5 -coated Si_3N_4 after corrosion in $\text{Na}_2\text{SO}_4 + \text{O}_2$ at 1000°C for 5 h prior to washing.

Fig. 6. XRD patterns of Ta₂O₅-coated Si₃N₄: (a) as-deposited; (b) after corrosion in Na₂SO₄ + O₂ at 1000°C for 5 h, but prior to washing in water; and (c) after washing.

and (b)] revealed that the Ta₂O₅ coating was changed to crystalline NaTaO₃. Most peaks in Fig. 6(b) were assigned to NaTaO₃ although there were several unindexable, minor peaks. The EMPA and XRD results suggested that the reaction between Na₂SO₄ and Ta₂O₅ was relatively fast at 1000°C:

Although NaTaO₃ is a thermodynamically favored compound to form in the presence of excess Na₂O according to the Ta₂O₅-Na₂O binary phase diagram,³ the rapid formation of NaTaO₃ is somewhat surprising since the eutectic point of this binary system is 1625°C, which is well above 1000°C used in the corrosion test. Since the melting point of NaTaO₃ is 1810°C, the NaTaO₃ layer was not expected to be molten during the corrosion treatment. The coefficient of thermal expansion (CTE) of NaTaO₃ is not known. However, any substantial change in CTE due to the Ta₂O₅-to-NaTaO₃ transition could contribute to the poor adherence exhibited by the reacted coating layer.

This sample gained 6.2 mg between the coating and corrosion steps. Alternately, assuming Eq. (1) as the major reaction and using the original weight gain of the coating (i.e., 3.0 mg), it was calculated that the formation of NaTaO₃ would result in a weight gain of only 3.8 mg. Thus, it appeared that the reacted coating layer contained a phase(s) other than NaTaO₃. This phase should be amorphous since it was mostly transparent to XRD. Also, the amorphous phase was not expected to simply be an unreacted portion of Na₂SO₄ since the pure Na₂SO₄ phase tended to crystallize even at 200°C as shown in Fig. 3(c). When this sample was subsequently washed in warm water, it lost 9.6 mg which was slightly higher than the combined weight gain due to the coating and corrosion steps (i.e., 0.4-mg weight loss relative to the initial weight of the substrate prior to coating).

The weight loss data were in agreement with EMPA and XRD data. Figure 7 shows that, upon washing, the corroded Ta₂O₅ layer was removed from the substrate except for the trace amounts of Ta and Na at the substrate surface. The XRD pattern of this sample obtained after washing [Fig. 6(c)] was basically that of a blank Si₃N₄ substrate [see Fig. 3(a)]. A previous investigation involving NaTaO₃ (ref. 4) implied that NaTaO₃ was not soluble in water. Perhaps it could be explained that the amorphous portion of the reacted coating layer was water soluble. Thus, when the amorphous phase was being dissolved in water, the NaTaO₃ phase was also released from the substrate. Currently, the Ta₂O₅-coated specimens which were exposed to longer corrosion treatments are being microstructurally evaluated.

(2) Burner Rig Sample Preparation

AlliedSignal Engines has provided ORNL with 25 NT154 Si₃N₄ flexure specimens which are to be coated with Ta₂O₅ at ORNL and subsequently burner rig tested at AlliedSignal. Since the NT154 specimens (10.2 x 1.3 x 0.6 cm) were much larger than GN10 substrates (1.0 x 0.4 x 0.3 cm) used in our previous work,

Fig. 7. Backscattered cross section image and elemental X-ray maps of Ta_2O_5 -coated Si_3N_4 after corrosion in $\text{Na}_2\text{SO}_4 + \text{O}_2$ at 1000°C for 5 h after washing.

the reactor heating arrangement was modified to increase the uniform deposition zone in the reactor. The length of the graphite susceptor was increased from 6.4 to 12.7 cm. A new RF coil was designed and installed to provide sufficient power to compensate for the increased susceptor length and also to achieve uniform temperature distribution along the axial direction of the reactor. As can be seen from Fig. 8, these changes significantly reduced the magnitude of axial temperature gradients, thus extending the length of uniform temperature zone from 5 to 10 cm. As shown in Fig. 9, a special quartz holder was designed and constructed to hold an NT154 substrate along the direction of gas flow.

For preliminary evaluation at AlliedSignal, three NT154 specimens were coated with Ta₂O₅ at a deposition temperature of 1250°C. One of the NT154 specimens, along with two GN10 substrates coated with Ta₂O₅, are shown in Fig. 10. As evident from the picture, the coating was uniform and well adhered to the NT154 substrate. Note that the area which was used to grip the substrate (about 1 cm) was not coated with Ta₂O₅. However, this area will not be exposed to the hot gas stream during the burner-rig testing. XRD was used to verify that the coatings on the NT154 substrates were pure Ta₂O₅. The coated NT154 specimens have been burner-rig tested at AlliedSignal, and the results are being analyzed.

Status of milestones

On schedule.

Publications

None.

References

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Fig. 8. Axial temperature profiles measured with a thermocouple before (a) and after (b) modifying susceptor length and RF coil configuration.

Fig. 9. A new holder was designed and used to place the NT154 substrate along the direction flow in the CVD reactor.

Fig. 10. NT154 and GN10 substrates coated with Ta_2O_5 .

Development of Adherent Coatings to Reduce Contact
Stress Damage of Ceramics
V. K. Sarin (Boston University)

Objective/Scope

The development of oxidation/corrosion resistant, high toughness, adherent coating configurations for silicon based ceramic substrates for use in advanced gas turbine engines.

Technical Progress

Annealing studies were done on SiC and Si₃N₄ substrates with Al₂O₃ coatings. The samples were heated to 1400°C for different times. TEM study of the annealed specimens indicated the formation of SiO₂ at the interface in the form of two layers; an amorphous silica layer immediately next to the substrate, and a crystalline silica layer between the amorphous silica layer and the Al₂O₃ coating. Cracks were observed in the crystalline SiO₂ layer indicating crystalline silica layer may be responsible for coating delamination. This was discussed in detail in the previous semiannual report.

To better understand this effect, amorphous CVD-SiO₂ coatings were grown on SiC substrates. The thickness of the coatings was approximately 1 μm. The precursor used was TEOS. Normal x-ray diffraction analysis indicated that the coatings were amorphous. They were then subjected to various degrees of heat treatment starting at 1200°C up to 1500°C for short periods of time to observe the transformation with temperature. Figure 1 shows the as-deposited SiO₂ coating on SiC.

The coatings remained intact when heated up to 2 hours at 1200, and 1300°C. At 1400°C, localized cracking with small areas of spallation of the coating was observed (Figure 2). The localized spallation appears to be at two different levels; at the coating/substrate interface, and at an intermediate level within the coating. When heated to 1500°C for 2 hours, coating delamination with a network of cracks, and localized spallation was observed (Figure 3). The extent of the cracks points out to the fact that there may be thermal stresses within different levels of the coating,

Figure 1: As deposited SiO₂ coating on SiC substrate

a)

b)

Figure 2: SiO₂ coating on SiC heated to 1400°C for 2 hours
a) Surface, b) Cross-section

Figure 3: SiO₂ coating on SiC heated to 1500°C for 2 hours
a) Surface, b) Cross-section

further indicating that there may be phase transformations within the coating. When the heat treatment was continued to 6 hours at 1500°C, major delamination of the coating was observed. The extent of the cracks points out to the fact that there may be thermal stresses within different levels of the coating due to phase transformations within the coating.

X-ray analysis was performed on samples with different levels of heat treatment. Figure 4 shows the x-ray diffraction patterns of these samples. As can be seen, the coating remains amorphous up to 1300°C (only β -SiC substrate peaks seen), cristobalite starts to form at approximately 1400°C, and is prevalent at 1500°C. This further reinforces our earlier theory that the cracking at the coating/substrate interface during heat treatment at 1400°C is due to phase transformation within the SiO₂ coating, resulting in volumetric changes.

Residual stresses in the coating due to growth and thermal mismatch were believed to effect the transformation of the coatings. Preliminary heat treatment studies were carried out on 0.02 μ m size amorphous SiO₂ powders to understand the effect of stresses on the transformation. Compressive stress to the level of 10,000 psi was applied to the powders before being heated. Plain and stressed powders were heated to various temperatures ranging from 1000 to 1500 °C and duration of 5 to 48 hours. The powder goes through a phase of densification via sintering before it transforms into cristobalite. Figure 5 shows SEM micrographs showing the various levels of transformation of the powders. Figures 6 and 7 show x-ray diffraction patterns illustrating the effect of stresses on the level of transformation of these powders. There is a marked increase in the intensity of the cristobalite peak when the powders were stressed. This clearly shows that the stresses promote the amorphous to crystalline transformation. Analysis with the help of computer models^[1] is being performed on the SiO₂/Al₂O₃ coating system to identify the level of residual stresses in these coatings. This information can then be used to design heat treatment experiments to obtain quantitative information on the effect of residual stresses on transformation. Based on these results, coatings can be designed accordingly to avoid or at the least minimize the transformation thus preventing the observed cracking of the multi-layered coatings.

Equilibrium thermodynamic analysis was performed on AlCl₃-SiCl₄-CO₂-H₂ system. Figure 8 shows ternary CVD phase diagrams of AlCl₃-SiCl₄-CO₂ system at 1000 °C and 2 and 75 torr. The ratio of H₂:(AlCl₃+SiCl₄+CO₂) is maintained at 5:1. To avoid excess Carbon in the deposit, it is evident that one needs to operate in the regime where there is excess CO₂

Figure 4: X-Ray Diffraction patterns for a) as-deposited, b) heat treated to 1300°C, and c) heat treated to 1500°C

Figure 5: Scanning Electron Micrographs of SiO₂ powder
a) amorphous, b) densified via sintering, c) partially transformed, and d) completely crystalline

Figure 6: X-ray diffraction pattern on silica powder heated to 1300 °C and 24 hours a) plain, and b) stressed

Figure 7: X-ray diffraction pattern on silica powder heated to 1400 °C and 10 hours a) plain, and b) stressed

Figure 8 : Ternary phase diagrams of $AlCl_3$ - $SiCl_4$ - CO_2 system at 1000 °C and a) 2 torr, and b) 75 torr

available for reaction. The excess carbon towards the left portion of the diagram is due to the fact that there aren't enough O_2 molecules available in the reaction to form the gaseous bi-product, CO. The phase plots show that lower pressures are preferred for obtaining carbon-free deposits. This is due to the fact that at lower pressures, carbon has a higher affinity to form gaseous products such as CH_4 than forming a solid deposit. No region of pure Mullite is obtained under these conditions, however it was found that the lower the process pressure the larger was the Mullite+ SiO_2 region. From these results reactant gas composition of $AlCl_3$ and $SiCl_4$ were varied (mole fractions from 10^{-5} to 1) keeping the $CO_2:H_2$ ratio at 1:2 to narrow the composition range. The resulting phase plot is as shown in Figure 9. The phase plot shows that Mullite can be obtained with these starting reactants if the stoichiometry of $AlCl_3:SiCl_4$ is maintained at the same level as that of Mullite ($Al:Si = 3:1$). It should be noted that any deviation from this input stoichiometry results in excess Al_2O_3 or SiO_2 . Since excess SiO_2 in Mullite is detrimental to elevated temperature properties of these coatings, it is critical to ensure no SiO_2 is obtained. This can be achieved, as indicated by the CVD phase diagram by shifting the input reactant stoichiometry a little to the Al rich side. Based on these results initial process parameters were established for experimentation.

References

1. D. Doppalapudi, R. Mulpuri, S.N. Basu, and V.K. Sarin, to be published.

Status of Milestones

	<u>Schedule</u>	<u>Status</u>
<u>Task 1</u> : Development of Al_2O_3/SiO_2 coatings.	5/94	On Schedule
<u>Task 2</u> : Coating Characterization for selection of best technique from Task 1.	7/94	On Schedule
<u>Task 3</u> : Development of the complete coating configuration for contact stress, oxidation and corrosion resistance evaluation.	9/94	On Schedule

Figure 9: CVD phase diagram of AlCl_3 - SiCl_4 - CO_2 - H_2 system at 1000 °C and 75 torr

Wear-Resistant Coatings

M. H. Haselkorn (Caterpillar Inc.)

Objective/Scope

The goal of this technical program is to develop wear-resistant coatings for piston ring and cylinder liner components for low heat-loss diesel engines.

Friction and wear screening in Phase I identified plasma sprayed high carbon iron-molybdenum and chromia-silica coatings as candidate piston ring wear coatings. Plasma sprayed chromia-silica and high carbon iron-molybdenum coatings, as well as, a low temperature arc vapor deposited (LTAVD) chrome nitride coating were identified as candidate cylinder liner wear coatings. The cast iron porcelain enamel coatings exhibited unsatisfactory wear rates because of porosity in the coating.

The three main technical tasks for Phase II are further optimization of the LTAVD chrome nitride and of the cast iron porcelain enamel wear coatings and the process scale-up of wear-resistant plasma coatings for cylinder liners.

The optimization of the LTAVD chrome nitride coating involves the development of an adherent 15 micron thick coating which meets the friction and wear goals of this program. The cast iron porcelain enamel process optimization centers on developing a CIPE composition with a minimum of porosity. The process scale-up of the plasma coatings will first develop I.D. plasma spray parameters for coating cylinder liners. Next, simulated cylinder liner specimens will be coated and the friction and wear properties of these coatings will be determined using reciprocating friction and wear testing using both new and "used" engine oil.

Technical Progress

Task 8, Process Scale-up of Wear-Resistant Plasma Coatings for Cylinder Liners, is completed. Statistical experiments, which determined the effect of primary gas flow, current, voltage, spray distance and carrier flow on coating microstructure and hardness and deposition efficiency, were used to build a predictive model to select three sets of I.D. plasma spray parameters for each powder. These parameters were then used to plasma spray Hohman A-6 friction and wear specimens. The coating parameters selected for each powder produced the best combination of plasma spray microstructure, coating hardness and highest deposition efficiencies.

The Hohman friction and wear characterization showed that varying the plasma spray parameters for the chromia-silica powder had little influence on the friction and wear performance of this powder. For this reason, the plasma spray parameters selected for the application of the chromia-silica powder to the inner diameter of the simulated diesel engine cylinder liners were those which result in the highest deposition efficiency.

The friction and wear properties of the high carbon iron-molybdenum powder were influenced by the application parameters. For this reason, the plasma spray parameters selected for this powder were those which produced the coating with the best friction and wear properties.

Prior to application of the plasma spray coatings to the inner diameter of the cylinder liners, machining is required to accommodate the coating thickness. The machining of 12 cylinder liners has been completed. This procedure required the fabrication of a special fixture for holding the liners.

Using the plasma spray parameters identified in Task 8, the chromia-silica and high carbon iron-molybdenum powders were applied to the bores of cylinder liners (12 liners were coated with each powder).

The inner diameters (I.D.) of the plasma sprayed cylinders were then finished machined to the proper dimensional tolerances using either a Heald 2EF Centernal Multi-Surface horizontal O.D./I.D. grinder at Caterpillar or a Okuma GI-20N O.D./I.D. grinder at Norton Company.

In Task 8C the machining parameters which produced the optimum surface finish and highest material removal rates were identified for coatings of each powder. Using these results as a guide, machining parameters (grinding wheel composition, feeds, speeds and depth of cut) were selected for each powder. The parameters selected included one set which would produce a high material removal rate and, one set with a lower material removal rate, but would produce a smoother surface finish. The material removal rates selected for each powder were:

Chromia-silica	—	0.50 and 9.04 mm ³ /min/mm,
High carbon iron-molybdenum	—	10.03 and 18.08 mm ³ /min/mm.

Only one grinding wheel composition was used to machine the plasma sprayed chromia-silica liners. The wheel selected contained 90 micron diamond grit in a vitreous bond. The increased material removal rates were obtained by increasing both the depth of cut (DOC) and feed rate.

Two CBN grinding wheel compositions were used for machining the plasma sprayed high carbon iron-molybdenum liners. A 15 micron CBN resinoid bonded wheel was used to achieve the optimum surface finish. The increased material removal rates were obtained by using a 52 micron vitreous bonded CBN wheel in combination with increased DOCs and feed rates.

Machining Results — Heald 2EF Centernal Multisurface O.D./I.D. Grinder

Similar surface finishes were obtained with the chromia-silica powder irrespective of which set of machining parameters were used. The largest difference observed with the two sets of parameters was the time required to machine the liner. Using the higher material removal rates, a liner could be machined in six minutes, compared to 24 minutes for the lower material removal rates. It is interesting to note that even with the higher material removal rate the force on the grinding wheel was very low suggesting that even higher material removal rates can be used with this powder.

The surface finish obtained machining the high carbon iron-molybdenum powder was affected by material removal rate. The low material removal rates produced a surface finish which was within the range required for the desired tribological properties. However, the surface obtained with the higher material removal rates was unacceptable. Scanning electron photomicrographs of the surface after machining showed the reason for the unacceptable surface finishes was that the higher material removal rates caused spallation of the coating.

Machining Results — Okuma GI-20N O.D./I.D. Grinder

Increasing the material removal rate during the machining of the I.D. of the chromia-silica plasma sprayed liners reduced the time required to machine the liners from 36 to 7.6 minutes. In addition, both the Ra (roughness average) and Rk (depth of roughness core profile, or the part of the surface after break-in which will carry the load and influence life and performance) of both surfaces, irrespective of the machining used, were essentially equal. However, increasing the DOC and feed rates did increase both power consumption (0.8 to 1.4 KW) and grinding wheel wear (0.013 to 0.038 mm on the diameter).

Changing both the CBN grit size, grinding wheel bond type, DOC and feedrate during the machining of the plasma sprayed high carbon iron-molybdenum liners reduced the machining time from 47 to 7.2 minutes. Again these changes had very little affect on either Ra and Rk of the machined surfaces. However, switching from a resonoid to a vitreous bonded grinding wheel did significantly reduce the amount of grinding wheel wear, even though larger DOCs and feed rates were used with the vitreous bonded wheel. Finally, with the higher feed rates and larger DOCs there was a slight increase in power consumption.

After reviewing the encouraging results obtained with the with the 53 micron vitreous bonded CBN grinding wheel and the larger DOC and higher feed rates, an attempt was made to further reduce the machining time by increasing the feed rate at the larger DOC. While these changes reduced the time to machine the liner to 5.8 minutes, significantly higher Ra and Rk values were characteristic of these surfaces. The reason for the poorer surface quality was that these machining parameters caused excessive grinding wheel vibration during machining.

The plasma spraying and machining of both sets of chromia-silica and high carbon iron-molybdenum piston rings fabricated at Caterpillar have been completed. Cameron-Plint and Battelle's high temperature friction and wear rig specimens have been cut from both sets of rings. In addition, specimens for the Cameron-Plint and Battelle's high temperature friction and wear rig have been cut from all the plasma sprayed and machined chromia-silica and high carbon iron-molybdenum cylinder liners.

Reciprocating friction and wear testing of the simulated plasma sprayed piston rings and cylinder liner specimens at both Caterpillar (Cameron-Plint) and Battelle (high temperature friction and wear rig) is continuing. Testing is approximately two-thirds complete at Battelle and one-half complete at Caterpillar.

Thick Thermal Barrier Coating (TTBC) Systems for Low Heat Rejection Diesel Engines

M. B. Beardsley (Caterpillar Inc.)

Objective/Scope

The objective of this program is to advance the fundamental understanding of thick thermal barrier coating systems for application to low heat rejection diesel engine combustion chambers. Areas of TTBC technology that will be examined include powder characteristics and chemistry; bond coat composition; coating design, microstructure, and thickness as they affect properties; durability, and reliability; and TTBC "aging" effects (microstructural and property changes) under diesel engine operating conditions.

Technical Progress

TTBC POWDERS

The thermal conductivity of the HOSP 8% yttria-zirconia materials (lots 34547, 34302 and 34143), the spray dried & sintered 8% yttria-zirconia materials (lots 34850, 34992, and 34993), and the calcium titanate (lot 34849) have been determined for the as-sprayed and aged (500 hours at 800 C) conditions and are shown in Figures 1 to 3. Both the HOSP and spray dried & sintered materials have deposition efficiencies in the 40 to 50% range but the spray dried & sintered materials have significantly lower thermal conductivities. The lower thermal conductivity is due to the lower kW power levels used to spray the spray dried & sintered materials. Little differences in the as-sprayed and aged thermal conductivities are seen even for the calcium titanate material. This is somewhat surprising, particularly for the 34993 material which has high silica and alumina content. Aging does show an effect on the mechanical properties of the HOSP materials as outlined below.

DESIGN, DEPOSITION, AND CHARACTERIZATION

Tensile and compressive strength of the HOSP 8% yttria-zirconia materials, the spray dried and sintered 8% yttria-zirconia materials, and the calcium titanate have been determined. The compressive and tensile B50 strengths and elastic moduli of these materials are compared in Figures 4 to 6. The elastic moduli were determined by axial compression and tension testing using a tube specimen. The compressive and tensile strengths were determined using 4-pt. bending with 10 samples tested for each group.

Little difference in strength is seen between the three lots of HOSP material. The small difference seen in the compressive strength of the machined and as-sprayed specimens for the HOSP materials is due to plastic deformation of the substrate material. This was determined using a finite

Figure 1. Thermal conductivity of the three HOSP 8% yttria-zirconia materials are shown for both the as-sprayed and aged conditions.

Figure 2. Thermal conductivity of the spray dried & sintered 8% yttria-zirconia materials are shown for both the as-sprayed and aged conditions.

Figure 3. Thermal conductivity of the calcium titanate material is shown for both the as-sprayed and aged conditions.

Figure 4. The B50 4 pt. bend compressive strength of the HOSP and spray dried & sintered 8% yttria-zirconias and the calcium titanate are shown. Ten bars of each material were broken.

Figure 5. The B50 4 pt. bend tensile strength of the HOSP and spray dried & sintered 8% yttria-zirconias and the calcium titanate are shown. Ten bars of each material were broken.

Figure 6. The compressive and tensile elastic moduli of the HOSP and spray dried & sintered 8% yttria-zirconias and the calcium titanate are shown.

element analysis of the specimens for these materials. An elastic analysis was used to generate the data shown in Figure 4. The higher strength of the of the aged materials indicates a similar strengthening of the materials as has been seen in the fatigue testing at high temperature. This effect appears to be more pronounced for the compressive strength then for the tensile strength. This is probably due to the residual stress in the compressive specimen caused by the mismatch of the thermal expansion of the ceramic and substrate at the aging temperature.

Differences in the strengths of lot 34850, 34992, and 34993 can be attributed to the different impurity levels of the lots. Lot 34992 has low silica and alumina content, lot 34850 has higher silica content with low alumina content, and lot 34993 has high silica and alumina content. The strength of the materials follow this trend with the higher purity materials having higher strength. Aged compressive strength specimens for lots 34850, 34992 and 34993 have been tested but not yet analyzed because the modulus of the aged materials has not yet been determined. Axial specimens for determination of the compressive moduli of these materials are currently being aged.

Strength testing of the 24% ceria-zirconia, 20% yttria-zirconia, and mullite is underway.

DURABILITY/RELIABILITY

Compressive bending fatigue using composite metal/coating specimens has been completed for lots 34547, 34302, 34143, 34850, and 34993. The resulting stress-life curves are shown in Figures 7 to 11. The HOSP materials again show little difference in fatigue behavior and Figure 12 shows the results for the HOSP lots plotted together. Although the spray dried & sintered materials have lower static strength then the HOSP materials, they have a relatively flat slope to the fatigue curve. Testing of lots 34992, 34849, 34108, and 34209 is underway.

AGING EFFECTS

Aging of the HOSP, spray dried & sintered, and calcium titanate showed little effect on the thermal conductivity and tensile strength. The compressive strength of the HOSP materials did exhibit a significant increase and is thought to be due to the combination of the temperature effect and the stress cause be the thermal expansion difference between the coating and the stainless steel substrate used for the compressive 4 pt. bend specimen at the aging temperature.

The aging effect previously reported for 8% yttria-zirconia in axial compressive loading was further investigated to determine the effect of load at temperature on the tensile properties of this material. Samples of the material were held at a compressive static load of 300 MPa at 800 C for one hour. The tensile modulus of the material was measured before and after aging

Figure 7. The compressive fatigue response of lot 34547 of the HOSP 8% yttria-zirconia is shown. The testing was done using 4 pt. bend of a composite metal substrate/ceramic coating.

Figure 8. The compressive fatigue response of lot 34302 of the HOSP 8% yttria-zirconia is shown. The testing was done using 4 pt. bend of a composite metal substrate/ceramic coating.

Figure 9. The compressive fatigue response of lot 34143 of the HOSP 8% yttria-zirconia is shown. The testing was done using 4 pt. bend of a composite metal substrate/ceramic coating.

Figure 10. The compressive fatigue response of lot 34850 of the spray dried & sintered 8% yttria-zirconia is shown. The testing was done using 4 pt. bend of a composite metal substrate/ceramic coating.

Figure 11. The compressive fatigue response of lot 34993 of the spray dried & sintered 8% yttria-zirconia is shown. The testing was done using 4 pt. bend of a composite metal substrate/ceramic coating.

Figure 12. The combine compressive fatigue response of the three lots of HOSP 8% yttria-zirconia is shown.

and showed a significant increase in the room temperature tensile modulus, Figure 13. This result and the temperature-only aging tests indicate that both temperature and load are required before significant aging effects are seen.

Axial load aging tests of the 24% ceria-zirconia material has been completed. The compressive modulus of the material was measured at room temperature in the as-sprayed condition and after holding at 200 MPa for 1 hour at 800 C. The elastic modulus of the material did not change for the aged condition as shown in Figure 14; unlike the 8% yttria-zirconia which showed a modulus increase after aging a 300 MPa for 1 hour at 800 C. The lower stress used for the 24% ceria-zirconia material was the result of the lower strength of the material.

Axial load aging of the calcium titanate material was not completed due to failure of the specimens during sample preparation. New samples have been sprayed with thicker gauge sections in order to prevent the specimen failures during the machining and etching process.

Status of Milestones

All milestones are on schedule.

Publications

None

Figure 13. The tensile elastic modulus of the yttria-zirconia after aging at a compressive static load of 300 MPa at 800 C for one hour. Note the increase in the tensile modulus similar to that previously seen for the compressive modulus.

Figure 14. The compressive elastic modulus of the 24% ceria-zirconia did not change after aging at a static load of 200 MPa at 800 C for one hour. (The before and aged curves fall on top of each other.)

1.4 JOINING

1.4.1 Ceramic-Metal Joints

Joining of Ceramics for Heat Engine Applications

M. L. Santella (Oak Ridge National Laboratory)

Objective/scope

The objective of this task is to develop strong, reliable joints containing ceramic components for applications in advanced heat engines. The overall emphasis of this task is on studying the brazing characteristics of silicon nitride and silicon carbide. The techniques of direct brazing as well as vapor coating ceramics to circumvent wetting problems are being applied to these materials. The planned activities during FY 1994 will include continuing the study of both the high-temperature brazing of silicon nitride and the mechanical behavior of braze joints. The work will encompass further evaluation and application of an analysis package and approach developed specifically for silicon nitride-to-metal braze joints and evaluating nonmetallic bonding materials for joining silicon nitride.

Technical highlights

Si₃N₄-to-metal brazing: A design for a poppet valve that combines an Si₃N₄ valve head with a metal stem was developed, and the proposed configuration was prepared for meshing and analysis using finite element techniques. The overall valve shape and dimensions closely approximate those of exhaust valves in small-block GM engines. The exact configuration of the valve cannot be disclosed at the present time, but it was chosen in an attempt to help minimize both residual stresses after brazing and mechanical loading of the braze layer and to provide for ease of fabrication. The finite element model of the proposed design contains over 10,000 elements.

The objective for the analysis was to provide guidance on how the properties of the ceramic and metal and the brazing temperature influence residual stress magnitude and location. Initial work on the selected design verified that the geometric model was acceptable for further analysis. A solution of the complete problem was then run using PY6 properties for the Si₃N₄, Alloy 909 (a controlled-expansion alloy) properties for the metal stem, and the properties of a gold-based alloy for the braze filler metal layer. These properties were used because they were readily available and representative of the materials of interest. The valve was assumed to be in a stress-free state at 830°C, which is a representative solidus temperature for a suitable braze filler metal. Upon cooling from this temperature to room temperature, residual stresses build up in the valve body due mainly to differences in the thermal expansion coefficients and elastic moduli of the various materials in the model.

Examination of interfaces between the Si₃N₄ head and the Alloy 909 stem showed regions of severe plastic flow in the braze layer and high residual stresses in the Si₃N₄. The braze layer was severely distorted because its relatively low yield strength and high ductility allowed it to accommodate much of the differential shrinkage. Residual tensile stresses that ranged up to near 400 MPa were predicted to develop in the Si₃N₄ head.

These results suggest that making a reliable valve of this configuration from these materials would be problematic.

The residual stresses in the Si_3N_4 are influenced by the various material properties, the geometry of the head and stem, and the processing conditions. Property data are being assembled to examine the effects of alternate materials. Reconsideration of the initial design and analysis of other factors are also anticipated as time and budget permit. When a design that appears viable in terms of residual stresses, processing, and economic considerations is found, prototypes for preliminary testing will be fabricated.

Status of milestones

- 141112 Report on initial evaluation of the wetting and melting characteristics of mixed oxide and oxynitride glasses on Si_3N_4 .
Completed: January 31, 1994

Publications

None.

Unpublished work

None.

1.5 CERAMIC MACHINING

Cost-Effective Ceramic Machining

P. J. Blau (Oak Ridge National Laboratory)

Objective/scope

The objective of this effort is to develop, in conjunction with U.S. industry, advanced technologies and the associated scientific and economic concepts necessary to reduce the costs associated with the machining of structural ceramics, especially as related to the use of these materials in energy-efficient, low-emissions transportation systems. This effort consists of subcontracts to industry and in-house research at Oak Ridge National Laboratory (ORNL), Argonne National Laboratory, and the National Institute of Standards and Technology. Progress reports for other than the ORNL in-house research portion of this work may be found elsewhere in this publication. The five subtasks in this effort are:

1. Environmental Safety and Health Aspects of Ceramic Machining,
2. Technology Assessment and Future Needs,
3. Advanced Machining Methods Development,
4. Ceramic Machinability and Related Performance, and
5. Structure and Surface Quality of Machined Ceramics.

The ORNL in-house research is aimed at two technical areas: (1) investigating the effects of machining practices on the durability of ceramics for valve and valve seat applications and (2) understanding and characterizing the detailed nature of machining-induced surface and sub-surface damage and their evolution in advanced ceramic materials using a range of analytical tools.

Technical highlights

Ten unsolicited research suggestions concerning cost-effective ceramics machining were reviewed by a group of five ORNL and Y-12 staff engineers for possible funding. Several of them showed promise, and future project ideas are under development in discussions with the submitters.

Tiles of NCX-5102 silicon nitride were machined by Chand-Kare Inc., Worcester, Massachusetts, under seven conditions to investigate the effect of machining parameters on repetitive impact wear behavior. Surface roughness parameters of one of the seven tiles has been measured using three different methods: mechanical stylus instrument, non-contact IR-laser, and atomic force microscope. It was found that the non-contact laser instrument gave significantly higher surface roughness parameters than the other techniques. The reasons for this difference are being evaluated.

In a cooperative effort, J. Bjerke of Caterpillar Technical Center, Peoria, Illinois, has been measuring the residual stresses of variously machined specimens which have been subjected to repetitive impact tests. The specimens were supplied by Eaton Corporation's Technical Center. Figure 1 shows that the impact wear damage (crater area) decreases with increasing compressive stress. A joint ORNL/Caterpillar article describing this work has been prepared for submission to the *Journal of Materials Research*. Its title is "Effect of Machining Residual Stresses on the Repetitive Impact Behavior of Silicon Nitride."

Fig. 1. Illustrating the positive effects of compressive stress on lowering repetitive impact damage in Eaton Corporation's sintered reaction-bonded silicon nitride (SRBSN). Data for specimens machined in various ways indicate the general trend. The impact crater size on a comparable polished specimen is indicated at the lower left (from ref. 2).

Surface damage studies using the new Leitz scanning acoustic microscope continue. A paper on the application of the technique to wear and scratch damage to various materials is being prepared by P. J. Blau and W. A. Simpson, Jr., for the 1995 International Conference on Wear of Materials. Its title is "Applications of Scanning Acoustic Microscopy in Analyzing Wear and Single Point Abrasion Damage."

Future plans

Work will continue on repetitive impact testing of variously machined NCX-5102 specimens.

Work will continue on comparing surface roughness measurements of ceramic parts obtained by different methods.

A new request for proposal for a competitive subcontract on grinding wheel technology has been prepared and will be released during the next few months.

Further studies of optimizing acoustic microscopy for ceramic machining studies will be conducted.

Status of milestones

On schedule.

Communications/visitors/travels

R. B. Schulz, D. R. Johnson, and P. J. Blau traveled to Dearborn, Michigan, on February 24, 1994, to brief the USCAR, U.S. Automotive Materials Partnership, newly formed Ceramics Committee about both the Cost-Effective Ceramic Machining Project and the Ceramic Technology Project.

M. Savitz and F. Davis, AlliedSignal Corp., visited ORNL on March 25, 1994, to discuss future ceramic machining-related program opportunities.

Problems encountered

None.

Publications/presentations

1. S. R. Srinivasan and P. J. Blau, "Effect of Relative Humidity on the Repetitive Impact Behavior of Machined Silicon Nitride Surfaces," *J. Am. Ceram. Soc.*, **77**(3), 683-88 (1994).
2. S. Srinivasan, P. J. Blau, and J. L. Bjerke, "Effect of Machining Residual Stresses on the Repetitive Impact Behavior of Silicon Nitride," to be submitted to the *J. Mater. Res.* (1994).
3. P. J. Blau and W. A. Simpson, Jr., 1994, "Applications of Scanning Acoustic Microscopy in Analyzing Wear and Single-Point Abrasion Damage," submitted to the International Wear of Materials Conference '95, Boston, Massachusetts.

*Innovative Grinding Wheel Design
for Cost-Effective Machining of Advanced Ceramics*

R.H. Licht, S. Ramanath, M. Simpson and E. Lilley (Norton Company)

Objective/Scope

The objectives of the Phase 1 program are: to define requirements, design, develop and evaluate a next-generation grinding wheel for cost-effective cylindrical grinding of advanced ceramics.

Ceramic machining, predominantly diamond grinding, is a major cost factor in advanced ceramics manufacturing. The abrasive wheel performance significantly influences the grinding costs. Additionally, the quality of the grinding operation greatly affects ceramic surface integrity, tolerance and manufacturing yield.

This program is a cooperative effort involving three Norton groups. The Norton Company Superabrasives Division will design and develop a novel metal bond system, and perform the wheel tests at the Norton World Grinding Technology Center. Norton Diamond Film Division will conduct a parallel and complementary research and development effort that incorporates a chemical vapor deposition (CVD) diamond film wheel system. The Northboro Research and Development Center (NRDC) will supply ceramic specimens for the grinding tests, and evaluate surface integrity in the ground ceramics.

The parallel path approach will be carried out in Task 1, Analysis of Required Grinding Wheel Characteristics. This task will involve the design of the bond with respect to mechanical and thermal characteristics, and the selection of the diamond grit. Task 1 will culminate in a small-wheel screening test involving controlled feed plunge grinding of sialon test disks.

Task 2, Design and Prototype Development, will down-select to a few wheel types for further design and optimization. Eight-inch (203 mm) diameter prototype wheels will be tested in a cylindrical mode, grinding ceramic rod specimens similar in geometry to valve stems. Grinding wheel performance will be assessed on three types of ceramic specimens: NC-520 sialon, NCX-5102 HIP'ed silicon nitride and AZ67H zirconia toughened alumina. Wheels will be evaluated for grinding parameters such as stock removal rate, wheel wear, G ratio, and grinding power. Additionally, the grinding wheel influence on ceramic surface integrity characteristics such as surface finish, damage and retained strength will be evaluated.

Technical Progress

Task 1.1: Requirements Definition and Experimental Design

General Wheel Design - Advanced ceramic components such as silicon nitride valves for automotive engines are machined to final shape and size predominantly by precision grinding using wheels containing diamond and occasionally cubic boron nitride abrasives (superabrasives). The requirements of cost-effective grinding wheels include the ability to grind work material at high removal rates, consume low levels of power, maintain low power levels for extended periods, produce quality workpieces with surface integrity, and have sufficient durability to maintain its form (if any) for extended periods, thereby requiring infrequent truing and dressing.

A consulting agreement was established with Professor Trevor Howes, University of

Connecticut Center for Grinding R&D (CGRD). Norton researchers visited the CGRD to discuss Superabrasives and CVD wheel design with regard to system stiffness, coolant absorption and thermal characteristics.

Superabrasive Wheel Bond Development -- There are primarily three major bond types that hold the abrasives: resin, glass or vitrified and metal bond. While resin bond products are good starting points for grinding a wide range of advanced ceramics producing quality surfaces with good part strength, they do not possess adequate life, requiring frequent truing and dressing. Vitrified or glass bonded products can provide better life but need to be handled with caution due to the extremely brittle nature and low strength of the bond matrix. They also pose considerable limitations for use in high speed grinding, a technology that is currently evolving. Conversely, conventional metal bonds have been found to be exceptionally durable and consume more power in grinding fine grain size ceramics, requiring frequent dressing to remove the worn abrasives, and expose sharp ones. Hence, the focus of bond design is to identify metal systems that possess the attributes of current resin and metal bonds. Metal bonds also include single layer products.

We pursued a "systems approach" during the bond design stage that looked at machine tool parameters, work material properties, wheel selection and operational factors. One of the requirements of a good bond design is matching the controlled wear of the abrasives to that of the bond holding them. To do this, we designed and set up a tester that determines the abrasive wear of several bond compositions. The wear tester pushes samples of bond compositions (not containing abrasive) at a constant load against an abrasive disk rotating at a constant speed. To establish a baseline and design criteria for an improved wheel development, we have tested standard resin (Norton DB 70) and metal bonds (Norton DM 112 and DM 17). The resin bond is currently used for ceramics grinding, while the metal bonds are generally considered too durable for this application. The results show that metal bonds, DM 112 and DM 17, are approximately six times more wear resistant than the DB 70 resin bond. The cumulative wear as a function of time of these bonds is shown in Figure 1. The flexural strength of existing resin and metal bonds, with no abrasives in them, were determined on 3 mm X 6.3 mm X 38 mm (0.12" x 0.25" x 1.5") specimens in a three-point bend fixture at crosshead speed of 5 mm/min. Figure 2 shows that the strength of a typical metal bond (DM 17 or DM 112) is approximately twice that of the resin bond. Thus, we established the upper and lower limits for bond wear resistance and strength.

A series of metal bond compositions that were designed to have intermediate values of abrasive wear and strength were fabricated and tested. These metal bond compositions were primarily based on DM 17 bond and contained different levels of porosity, produced by a pore inducer designated as PI2. Pores in grinding wheels serve several purposes; they increase the bond wear rates needed in existing metal bonds by lowering the contact area, reduce the friction between wheel and work thereby lowering spindle power requirements, provide a space for the ground ceramic chips ("chip clearance") and allow better application of grinding fluid that is essential for lubricity and heat transfer. The results in Figure 3 show that the increased porosity levels reduce the wear resistance of the bond. Figures 4 and 5 show results of wear tests of two other types of pore inducers (PI 1 and PI 3) at levels of 40% and 60% by volume respectively, which resulted in similar conclusions. We evaluated alternate approaches to induce porosity, but with less favorable results. These experimental bonds produced uncontrolled and variable porosity and thus will be discontinued.

Figure 1. Normalized cumulative abrasive wear vs. time for standard resin bond (DB 70) and metal bonds (DM 17 and DM 112).

Figure 2. Normalized 3-point bend strength of DB 70 resin and DM 112 metal bonds.

Figure 3. Normalized cumulative wear in abrasion wear test vs. time for experimental bonds with different levels of pore inducer, PI2. Standard resin and metal bonds are included for comparison.

Figure 4. Normalized cumulative wear in abrasion wear test vs. time for experimental bonds with 40 vol% of different pore inducers. Standard resin and metal bonds are included for comparison.

Figure 5. Normalized cumulative wear in abrasion wear test vs. time for experimental bonds with 60 vol% of different pore inducers. Standard resin and metal bonds are included for comparison.

Test bars of another patented bond family -- trade name Norton Alzan -- were also made and tested. The strength and wear resistance of the base Alzan bond was lower than that of resin bond, DB 70, and these properties decreased with increasing porosity. Therefore, this system, would not be expected to provide adequate wheel life for grinding of ceramics.

CVD Diamond Wheel - We reviewed with Prof. Howes, the requirements for a wheel that is stable with respect to the development of chatter and that is resistant to thermal failure of the diamond wheel bond, and we concluded the design for the first CVD test wheel. We expect the thermal performance of the CVD test wheel to be very good, perhaps obviating the need for a high degree of porosity to transport coolant. In our initial testing, we will not modulate the wheel stiffness to reduce chatter because we expect to be testing on a very rigid machine (although the harmonic response of the machine still needs to be characterized).

Selection of Abrasive Type, Size, and Concentration - The next important design consideration, after the design of bond type, is the selection of the appropriate type, size and concentration of abrasives. Superabrasives and the CVD diamond wheel research groups completed a preliminary design review to finalize the screening wheel test design. Size and specification standardization were done to assure meaningful grinding test comparisons.

The type of superabrasives to be used has been narrowed down to a few choices of diamond types based on work material requirements. One of the requirements for efficient ceramic grinding is the use of sharp abrasives. As the wheel is worn, the grinding forces on the abrasive grits must be sufficient enough to fracture them leading to new sharp cutting points, as opposed to development of attritious wear flats that could produce grinding damage in ceramics. We will focus on friable and weak diamond type abrasive. The size of the grits for initial Superabrasive wheel tests will be U.S. Mesh 270/325 (Norton 320 grit), which is recommended by our application engineers for reducing damage in general purpose rough-to-intermediate grinding of ceramics. The effective abrasive grit size for the CVD diamond wheels will also be 320 grit, (approximately 50 μ m diameter). Finish grinding abrasive specifications would depend on individual application needs of surface finish, part geometry, tolerances, etc. We fabricated all the superabrasive wheels at 100 concentration (25 volume percent diamond abrasives) with the exception of those where we want to study the effect of diamond concentration.

Task 1.2: Screening Test Wheel Manufacturing

Superabrasive Wheels -- The Task 1.1, 7.6 cm (3") screening wheel experimental design was completed, based on the results of strength and abrasive wear tests. We selected wheel variables for the 7.6 cm screening tests that include:

bond porosity levels	diamond abrasive types
type of pore inducers	diamond abrasive volume percent
solid lubricants	methods of processing
other bond compositions	process conditions (sintering temperature)
metal powders versus prealloys	single layer (MSL) type wheels.

The manufacturing of the 7.6 cm diameter x 1.3 cm thick x 2.2 cm hole (3" x 0.5" x 0.875") test wheels for initial screening test was completed. These wheels include the standard

metal bond and resin bond wheels. Several wheel manufacturing difficulties were encountered because of the extreme range of porosity levels in the experimental bonds. Initially, we selected a common core for all bonds, to maintain parameters such as core stiffness and thermal conductivity. This led to wheel-core separations, especially on wheels containing high levels of solid lubricants and porosity levels. These issues were resolved, and the remaining 7.6 cm superabrasive test wheels were manufactured. We expect to fabricate some additional 7.6 cm experimental wheels based on the preliminary grinding results.

CVD Diamond Wheels - The fixture for coating the abrasive elements of the CVD diamond wheel was designed and built. Mechanically, the fixture works well and has run for over 200 hours to date, coating the abrasive elements. We found diamond growth to be much lower than expected ($0.2 \mu\text{m/hr}$), therefore, 50 hours of deposition was needed to coat the elements to the required $10 \mu\text{m}$. We believe that the cause for the low rate is due to the low deposition temperature (estimated to be less than 800°C). It appears we need to reduce the spacing between the elements to be coated and the plasma torch used for coating. We plan to modify the fixture to bring the elements closer to the plasma torch. This may result in a different diamond microstructure and hence different grinding performance. We will test this new microstructure in a subsequent wheel.

We have assembled a test wheel using uncoated abrasive elements to develop this part of the process. Sectioning of the resulting wheel showed no significant porosity, even in locations where the abrasive elements were close together. The distribution of the abrasive was not as uniform as we would wish: there was a tendency for the abrasive elements to clump together. It is possible that this was exacerbated by the temperature used to fire the bond holding the abrasive elements together. In the future, we will lower the temperature and increase the firing time.

A 7.6 cm screening wheel is being assembled from the segments coated with diamond. This wheel will be tested in the screening test along with the Superabrasive test wheels.

NRDC Ceramics Support - The eighty-four NCX-520 sialon disks were fabricated, inspected and delivered for the grinding test. Twenty additional back-up discs are in process. Densities of the disks are within specification. Strength and toughness characterization are in process.

Task 1.3: Screening Wheel Grinding Test and Data Analysis

Norton reviewed machine-wheel stiffness issues with Professor Howes. We plan to have CGRD personnel conduct a "hammer test" on the screening test grinding machine-wheel system for both resin bonded and metal bonded wheels.

The screening tests of the 7.6 cm wheels in a plunge grinding mode have begun on an Okuma CNC cylindrical grinder. The test was originally proposed to be conducted on the CF grinder at known normal force levels. We selected the recently acquired Okuma machine because of its superior stiffness, spindle speed, controls, versatility and force measurement capabilities. The test is being conducted at controlled feed rates instead of controlled normal force levels. However, it will be possible to acquire all the information that would have been generated on the CF grinder, plus additional controlled feed information that is more consistent with current OD grinding practices.

The ceramic workpiece is in the form of a 11.2 cm diameter ring x 7 cm ID x 0.6 cm

thick mounted on a specially designed and manufactured arbor that, in turn, is located and mounted precisely on the machine. Thus, it is possible to remove the workpiece together with the arbor for the periodic examination of the ground surface, and to put it back on the machine at the same location. To maximize the testing data, we are conducting short grinds at two material removal rates on all wheels followed by longer runs on a selected few wheels. The workpieces will be examined and tested for grinding damage.

Task 2.2: Fabrication of 20.3 cm (8") Wheels and Ceramic Specimens -- The AZ67HS zirconia toughened alumina (ZTA) rods were completed by Norton Advanced Ceramics, (Export, PA). NRDC is performing mechanical property characterization for the ZTA rods. Fabrication of the NCX-520 sialon and NCX-5102 HIP'ed silicon nitride rods are in process at NRDC.

Status of Milestones

Milestone 1.1: Requirements definition and experimental design, is complete.

Milestone 1.2: Screening test wheel manufacturing, has been completed for the Superabrasive experimental wheels. Some additional wheels may be fabricated after review of the initial grinding results. Completion of the first CVD diamond grinding wheel is expected in April.

Milestone 1.3: The screening wheel test has started approximately one month behind schedule. This delay is not expected to affect the Task 2 schedule.

Milestone 2.2: Fabrication of the ceramic rods for the Task 2 grinding test is ahead of schedule.

Communications/Visits/Travel

R.H. Licht, S. Ramanath and M. Simpson visited the University of Connecticut to consult with Professor Trevor Howes, March 16, 1994.

Publications/presentations

R.H. Licht presented, "Development of the Next-Generation Grinding Wheel for Ceramics," at the Cost-Effective Ceramic Machining Project Review and Coordination Meeting, Oak Ridge, TN, September 8, 1993.

Cost-Effective Method for Determining the Grindability of Ceramics

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1 Objective/Scope

The objective of this program is to develop a cost-effective method to determine the grindability of ceramics leading to cost-effective methods for machining such ceramics. In this first phase of activity, Chand Kare Technical Ceramics is engaged in directing its efforts towards review of literature related to ceramic grinding, development of a variable definition of grindability, design of grindability test experiments, and design of a ceramics grindability test system (CGTS). The grindability study underway also includes establishment of correlation between the grindability number and the conventional grinding practices.

2 Technical Highlights

The technical progress to date is summarized by activities in the attached Milestone Schedule. The remainder of this section describes activity during the past six months which includes project planning, literature review, definition of grindability, characterization of diamond belt, and design of the test machine.

2.1 Literature Search and Study

Extensive literature search and study have been conducted during the past six months. The studied literature is listed in the appendix at the end of the report.

2.2 Definition of Grindability

In the following discussion, grindability has been defined from several aspects (productivity, cost and part quality). The advantages and disadvantages of each possible definition has been discussed. The most suitable definition will be chosen based on the basic requirements of grindability.

Grindability or machinability is probably best defined as a complex property of a material which controls the facility by which it may be machined to the size, shape, and surface finish required commercially. Unlike other material properties such as hardness, toughness, strength etc which are well defined and for which procedures exist to experimentally determine their values,

there exists no clear definition for "Grindability". If one material is said to be easier to grind than another, it could mean different things for different engineers with different interests. The meaning usually depends on the purpose of the research. It also tends to reflect the immediate interest of the user. People who concerned with surface finish problems tend to think in terms of 'finishability', others may consider that the term can be used to indicate how fast a material can be removed, while some may consider it to be a measure of the tool life or even cost. Machinability still tends to remain a term which means 'All things to all men' (Mills and Redford, 1983). The objective of the present research is to cost-effectively determine the grindability of ceramic materials. Therefore, an appropriate definition for grindability is needed. In this work, we will discuss grindability from various aspects in terms of productivity, part quality and cost. The merits and disadvantages of each possibility in defining grindability will be discussed. Based on the discussion, a definition which is most cost effective is proposed.

2.2.1 Basic Requirements for Grindability Definition

Before we start to discuss a definition for Grindability, it is necessary to consider the basic requirements for the grindability definition which will serve as guidelines for choosing the various options. It should be remembered that we are looking for a cost effective way. It is desirable that the testing procedure require only a minimum of time, material, and labor. Therefore, it should satisfy the following requirements: easy to experimentally obtain, cost effective, and sensitive to material property. Let us consider each of them separately.

A. Easy to experimentally obtain

The grindability of a material needs to be experimentally obtained. It should be defined in such a way that it can be obtained very easily. The experimental set-up should be simple. The experiment itself should be easy to conduct. The measurement of parameters needed to find the grindability should be also easy. The calculation after the measurements should be very simple.

B. Cost effective to obtain

Cost effectiveness is a very important aspect in evaluating grindability. Cost is closely related to how easy it can be obtained. The definition should satisfy the requirement that the experiment for determining the grindability of a new material can be done very quickly. The experiment should be so designed that no special training is needed for conducting the experiment. Also, the abrasive tool and specimen consumption should be small, and specimen preparation should be easy.

C. Sensitive to material properties

One of the purposes to conduct grindability test is to rank the ceramic materials in terms of ease with which they could be ground. The testing method has to be sensitive to small differences in grindability. Therefore the definition should be very sensitive to material properties. If two materials have very distinguished mechanical or thermal properties, it is expected that their grindability numbers will be significantly different. Therefore, the definition should be such that it will reveal the difference in material properties instead of other grinding parameters such as

workspeed, depth of cut etc.

2.2.2 Various Possibilities of Defining Grindability

In metal cutting, attempts to measure machinability are usually based upon determinations of tool wear, chip behavior, energy consumption, or rate of material removal. Grindability can also be addressed from various aspects, namely productivity, part quality and cost. For each aspect, it also can be defined in terms of different parameters. In this section, we will look at each of these aspects, and discuss the merits and disadvantages of all the possible definitions. After evaluating each definition using the basic requirements proposed above, the most suitable one will be chosen.

A. In terms of productivity

First, let us look at how to define grindability in terms of productivity. Volumetric material removal rate z_w (volume of material removed per unit time per unit width of grinding) is usually used as a measure of how fast the material can be removed. In grinding of metallic materials using conventional aluminum oxide wheels, this parameter is usually used to characterize a grinding process and compare grinding wheels, grinding fluids, and work materials. It is also used as a criteria to choose suitable grinding parameters such as wheelspeed, workspeed, depth of cut, and dressing conditions. Here the material removal rate will be used to discuss grindability of ceramic materials.

In terms of how the infeed is given or accomplished, grinding operations can be divided into two categories: controlled force grinding and controlled infeed grinding. In controlled force grinding, the normal grinding force is controlled to the predetermined value and the rate at which the material is removed depends on the material being ground. In controlled infeed grinding, the infeed (depth of cut) is kept constant and the normal force varies with work material. Now, let us consider both types of grinding and discuss its appropriateness for testing grindability.

Controlled Force Mode

First, let us look at the controlled force grinding in which the normal grinding force is kept constant by using a special grinder such as the one shown in Figure 1. The rate of downfeed achieved by grinding the material under test using an abrasive tool of predetermined form can be taken as a measure of the grindability of the material. For this controlled force grinding, the specimen can be held in two ways: horizontally as in Figure 1(a) or longitudinally as in Figure 1(b). If it is held horizontally as in Figure 1(a), the specimen can be ground with or without table traverse motion. Without table traverse motion, the pressure between the contact wheel and the specimen varies due to the contact length between the specimen and the contact wheel increases as the contact wheel cuts into the specimen as shown in Figure 2(a). The grinding condition varies during the test. There are two additional aspects which need to be considered with table traverse motion. First, how fast the traverse should be, and secondly, how to control the reverse at both ends of the specimen which both of which pose difficulties for testing.

If the specimen is held longitudinally as in Figure 1(b), no traverse motion is needed and

Figure 1 Illustration of controlled force grinding

Figure 2 Variation of contact lengths (a) holding specimen horizontally, (b) holding specimen longitudinally

also the grinding condition can be maintained unchanged during the test if the specimen is preformed to conform with the size of the contact wheel as shown in Figure 2(b). Therefore, holding the specimen longitudinally seems to be superior to holding it horizontally.

It is very simple to use controlled force grinding to determine grindability. Applying a predetermined normal force and grinding the material for a specified period time, more material will be removed if the ceramics is easier to grind, and less will be removed if it is difficult to grind. The amount of material removed will distinguish the grindability of all the materials. The mathematic definition of grindability in terms of material removal rate under controlled force grinding and the proposed experimental method for determining a material's grindability will be discussed later on.

Controlled infeed Mode

Most of the practical grinding operations are performed under controlled infeed grinding in which the downfeed (depth of cut) is controlled to the predetermined value (depth of cut 'a') during a grinding pass as in Figure 3. Under this condition and with other grinding conditions kept constant, the grinding forces and power needed to remove the given layer of material depends on the property of the material being ground. Higher forces and power will be experienced if the material is difficult to grind and lower forces and power will be experienced if the material is easy to grind. The magnitude of the forces and power (or specific energy which is defined as energy consumption per unit volume of material removal) can be used to distinguish the grindability of different materials.

One of the shortcomings of using controlled infeed grinding is that a force dynamometer is needed. A reliable one may be costly. Another problem is that the forces and power (specific energy) strongly depend on the mode of grinding, ductile or brittle. Usually, much smaller forces and power are experienced under brittle mode than under ductile mode. For ceramic materials, whether the grinding is under ductile or brittle mode depends more on the grinding conditions than on the material property. Most of the time, the grinding is conducted under a combination of both brittle and ductile modes. Therefore, it is also difficult to choose an appropriate grinding condition (depth of cut, workspeed) under which all the ceramic materials can be tested.

B. In Terms of Quality

When part quality is a problem, the grindability can also be discussed in terms of quality. However quality itself is a concept which needs to be clarified. Part quality can be addressed from various aspects. First of all, **Dimensional accuracy** is one aspect of the quality. While considering size and geometry accuracy from the point view of grindability, it means whether it is easy to obtain certain accuracy requirement for a part of certain material. Definitely, achieving certain size and geometry accuracy depends more on the machine accuracy and the part geometry itself than on the material property. For grinding of ceramic material, it should be relatively easier to achieve certain accuracy than for metallic materials because of the much higher elasticity E (Young's Modules) of ceramic materials. Secondly, **Surface Integrity**, which includes surface roughness, residual stress and burn mark, is another important aspect of quality. For ceramic grinding, residual stress is usually compressive, workpiece burn is rarely a problem because of

Figure 3 Illustration of controlled infeed grinding

much lower grinding temperature due to the much higher thermal conductivity of diamond abrasive and the higher temperature resistance of ceramic materials. Surface finish is usually difficult to obtain because of the brittle characteristics of ceramic materials. However, surface finish depends more on the grinding mode than on material property.

Part quality is definitely material related. It is easier to achieve certain quality requirement for some material than for others. However the machining quality is more related to the grinding machine used, grinding parameters chosen, and the company's practice than to material properties. Also, it will be very difficult to quantitatively characterize quality for the purpose of grindability. Part quality may not be very sensitive to material properties. It also posts higher requirements for grindability testing. Our conclusion is that quality is not suitable for defining a grindability which can be cost effectively obtained.

C. In Terms of Cost

Cost in terms of dollar values strongly depends on a company's situation such as management and labor cost etc. For the purpose of studying grindability, cost can be discussed in terms of machining time, power consumption, wheel consumption etc. Definitely, cost is closely related to productivity, but wheel cost is a big portion of the overall machining cost for most ceramic grinding. This can be characterized by considering how much ceramic material can be removed by consuming unit volume of diamond wheel. Therefore, G-ratio should be a good parameter to use for defining grindability in terms of cost. G-ratio, also called grinding ratio, is defined as the ratio of volumetric material removal rate to the volumetric wheel wear rate, or

$$G \equiv \frac{Z_w}{Z_s}$$

where z_w is the volumetric material removal rate per unit width of grinding ($\text{mm}^3/\text{mm second}$) and z_s is the volumetric wheel wear rate per unit width of grinding ($\text{mm}^3/\text{mm second}$).

G-ratio is a valuable parameter for evaluating various grinding wheels, grinding fluids and choosing optimum grinding conditions for grinding of metallic materials with conventional aluminum oxide wheels. It can also be used to compare and rank the grindability of ceramic materials. If G-ratio is high, material is considered to be easy to grind and otherwise it is considered to be difficult to grind. There are two difficulties using G-ratio as a measure of grindability of ceramic materials. First, it is very difficulty to measure the volumetric wear rate of a diamond wheel because of its much high wear resistance, thus making the test difficult. Secondly, it will be very time consuming to conduct test to measure G-ratio even for conventional abrasive wheels. Therefore, it not cost effective to use G-ratio to define grindability for ceramic grinding.

Summarizing the above discussion, we can conclude that grinding forces, power (or specific energies) obtained for controlled infeed grinding and surface finish depends more on the mode of grinding (brittle or ductile) than on the material itself. The mode of grinding depends more on the grinding condition than on the material. Therefore, these parameters are not suitable for defining grindability for evaluating material. From the cost point view, G-ratio should be

used. But it is not a cost effective definition either. Therefore, volumetric material removal rate obtained under controlled force grinding, which measures the rate of feed achieved per unit force, has been used to define the grindability of ceramic materials.

2.2.3 Mathematical Definition of Grindability

We have come to the conclusion that volumetric material removal rate per unit force obtained under controlled force grinding should be used to define the grindability of ceramic material. It should be noted that grindability is a material property. Therefore, the influence of other factors on material removal rate should be excluded from the definition. Under controlled force grinding, material removal rate should be a function of normal grinding force per unit width of grinding F_n , wheelspeed (or belt speed) v_s , material properties, and wheel (or belt) characteristics. If ϕ_c is a parameter which accounts for the influence of ceramic material property on material removal rate, and ϕ_d is a parameter which accounts for the influence of diamond wheel (or belt) characteristics on material removal rate, the material removal rate z_w (volumetric material removal per unit time per unit width of grinding) can be expressed as:

$$z_w = f(v_s, F_n, \phi_c, \phi_d) \quad (2)$$

If same kind of diamond belt is used for all the grindability tests, the influence of diamond belt on material removal rate can be excluded from equation (2). The material removal rate per unit normal grinding force is defined as the material removal parameter, or

$$\Lambda_w = \frac{\partial z_w}{\partial F_n} \quad (3)$$

Under controlled force grinding, material removal parameter Λ_w increases with wheelspeed v_s . In order to find a parameter which depends only on material property, we define

$$\lambda = \frac{\partial \Lambda_w}{\partial v_s} = \frac{\partial}{\partial v_s} \left(\frac{\partial z_w}{\partial F_n} \right) \quad (4)$$

which is the volumetric material removal rate per unit wheelspeed under unit normal grinding force.

For grinding of metallic materials with conventional aluminum oxide wheels, it has been found that the material removal rate is proportional to the normal force if the dominant material removal mechanism is cutting instead of plowing as in Figure 4(a). Therefore the material removal parameter Λ_w for a given wheelspeed is the slope of the corresponding line and does not depend on the normal grinding force. Under this condition, the material removal parameter is only related to the material property and wheelspeed (or belt speed). Researches under controlled force grinding have indicated that material removal rate is approximately proportional to the wheelspeed v_s . If this linear relationship still holds true for ceramic grinding, we have a parameter

Figure 4 Empirical relationship between normal force and material removal rate

which is only related to the material property, or

$$\lambda_w = \frac{z_w}{v_s F_n} = g(\phi_c) \quad (5)$$

which is the slope of the line in Figure 4(b). This parameter λ_w has a physical meaning. It represents the equivalent cross sectional area of a ribbon like strip of material being removed from the workpiece under unit normal force. This parameter can be used to distinguish the grindability of various ceramic materials because it only depends on material property. For easier material, parameter λ_w will be bigger, and for difficult material, it will be smaller. In the next section, we will discuss how to experimentally evaluate this normalized material parameter. After testing all the available ceramic materials, a result similar to what is given in Figure 5 will be obtained, with large λ_w value corresponding to materials easy to grind and smaller λ_w values corresponding to difficult to grind materials.

As a practical matter, it is necessary to choose an appropriate diamond belt to conduct all the grinding tests in order to obtain comparable testing result. This requirement may be difficult to satisfy because the diamond belt selected for some ceramic materials may not suitable for others. Analogous to Rockwell hardness testing in which different indentors (ball or cone) are used for materials of different hardness, different diamond belt may also be used to account for various ceramic materials. If so, the grindability of ceramic materials may need to be measured using different scales such as *grindability scale A, B or C* etc analogous to the Rockwell hardness definition.

After the belt is chosen, the appropriate normal force range and belt speed need to be determined. The belt speed commonly used in practice is about 30 m/s. A constant belt speed will be used in all the testings. It is desirable that all the tests be conducted under the same range of normal grinding force in order to obtain comparable results. But different range of normal force may need to be applied in order to successfully grind all the available materials. For materials which are easy to grind, smaller normal force should be used, and for materials which are difficulty to grind, larger normal force should be used. Under this condition, we can also define different grindability scales analogous Rockwell hardness scale A and C in which different loads are applied using the same indenter. If the material removal rate increases proportionally with the normal force as in Figure 4(a), extrapolation technique can be used to obtain comparable results under standard conditions.

For the purpose of ranking various ceramic materials in terms of this parameter λ_w , a reference material should be chosen. The reference material is chosen to be of reasonable grindability and of the same basic type as the test materials but, importantly, it is often chosen for the consistency of its grinding characteristics. For the reference material chosen, some grinding tests should be conducted to determine its λ_w value. If the grindability of the reference

Figure 5 Normalized material removal parameter versus different materials

material is specified as 10, the grindability of a new material can be expressed as:

$$C_g = \frac{\lambda_w}{\lambda_r} 10 = 10 \frac{z_w}{v_s F_n} \frac{1}{\lambda_r} \quad (6)$$

where C_g is the grindability of the tested material. After testing all the available ceramic materials and finding their grindabilities, the ease of grinding the new material can be compared with the grinding characteristics of the chosen reference material. For the reference material, extensive testing should be conducted to understand its process behavior during grinding. This test should be performed with diamond wheel instead of belt under regular pendulum grinding operation. The information obtained can be very useful to infer a set of reasonable grinding parameters for the new material.

If the grinding condition (belt speed, normal force and grinding width) is maintained constant from test to test, which is intended to accomplish in our test machine, the definition of grindability can be further simplified as:

$$C_G = \frac{z_{wt}}{z_{wr}} \cdot 10 \quad (7)$$

where z_{wt} is the volumetric material removal rate of the tested material and z_{wr} is the volumetric material removal rate of the reference material.

For a more comprehensive study, after the ranking test using diamond belt grinding, all the available materials should be ground using diamond wheels to obtain information about each material. For a future new material, conduct the grindability test and find its grindability. The obtained grindability is then compared with the calibrated grindability of various ceramic materials to see which known material this new material is similar to. From the known material, a set of suitable grinding parameters can then be obtained for the new material.

2.2.4 Multi-points test:

In order to obtain more accurate result, several data points should be used to evaluate parameter λ_w in equation (5). For this purpose, n tests should be conducted for each material under different normal grinding forces with a constant belt speed v_s . For test number i , normal force F_{ni} is applied and the specimen is ground for a period time of T . The accumulative volume of material removal per unit width of grinding is Q_{wi} . The average material removal rate can be calculated as:

$$z_{wi} = \frac{Q_{wi}}{T} \quad (8)$$

If the material removal rate is proportional to the applied normal grinding force as in grinding

of metallic materials with aluminum oxide wheels, the material removal parameter Λ_{wi} can be calculated by

$$\Lambda_{wi} = \frac{Z_{wi}}{F_{ni}} \quad (9)$$

and the normalized parameter λ_{wi} can be calculated by

$$\lambda_{wi} = \frac{\Lambda_{wi}}{v_s} \quad (10)$$

After the n grinding test for each material, we have the following data matrix which can be used to calculate the average value of the normalized parameter λ_w for the tested material by

$$\lambda_w = \frac{1}{n} \sum_{i=1}^n \lambda_{wi} \quad (11)$$

Test Data Matrix

Normal grinding force (N/mm)	F_n	F_{n1}	F_{n2}	F_{n3}	F_{n4}	$F_{n5} \dots F_{nn}$
Accumulative removal (mm^3/mm)	Q_w	Q_{w1}	Q_{w2}	Q_{w3}	Q_{w4}	$Q_{w5} \dots Q_{wn}$
Material removal rate ($\text{mm}^3/\text{mm s}$)	Z_w	Z_{w1}	Z_{w2}	Z_{w3}	Z_{w4}	$Z_{w5} \dots Z_{wn}$
Material removal parameter	Λ_w	Λ_{w1}	Λ_{w2}	Λ_{w3}	Λ_{w4}	$\Lambda_{w5} \dots \Lambda_{wn}$
Normalized parameter	λ_w	λ_{w1}	λ_{w2}	λ_{w3}	λ_{w4}	$\lambda_{w5} \dots \lambda_{wn}$

For more consistent testing result, T and F_{ni} should be specified in the manual. They should be the same as what will be used at Chand Kare Technical Ceramics for the calibration test. The technique used to measure the accumulative material removal will be discussed in the next section. It should be noted that different normal force values may be needed for different ceramic materials for a successful grinding. Experiments may be needed for a particular material to determine the suitable range of normal force values. The force value depends on material properties which will have influence on grindability.

2.2.5 Accumulative Volumetric Material Removal

For the controlled force grinding by holding the specimen longitudinally as in Figure 1(b), the accumulative material removal per unit width of grinding can be obtained as:

$$Q_w = A(l_i - l_f) \quad (12)$$

where l_i and l_f are the initial and final lengths of the specimen and A is the cross sectional area

of the specimen as shown in Figure 6. It should be noted that the specimen should be ground to conform with the contact wheel prior to the grindability test for more consistent grinding condition throughout the test.

2.3 Characterization of Diamond Belts

In order to obtain reliable and repeatable grindability result, it is very important that grinding conditions including process parameters (normal grinding force, belt speed) and characteristics of abrasive tools be controlled constant from test to test. The test machine will be designed to guarantee consistent process parameters. A belt wider than the specimen will be used in the test. The specimen will be indexed across the belt width after each test to fully utilize the belt as shown in Figure 7. Under this circumstance, it is important to know that a diamond belt has a uniform characteristics across its width. Also, it is important to know that belts from different batches have statistically the same characteristics. Therefore, it is necessary to evaluate diamond belts quantitatively. For this purpose, diamond belts will be characterized from geometric and dynamic grinding aspects respectively.

2.3.1 Geometric Characterization

The first step of characterizing a diamond belt is from the geometric aspect which includes belt thickness variations along the circumferential direction and wide direction, variation of cluster density on the belt surface, size variation of cluster area, variation diamond grit distribution density within each individual cluster.

A. Belt thickness variations along circumference (length) and width

A schematic illustration of diamond belt surface is given in Figure 8. The belt consists of circular diamond clusters. Each diamond cluster includes a number of diamond grits. The thickness variation along circumference may have influence on the stability of belt motion, which may further influence the stability of grinding process.

B. Variation of cluster density

At any given belt speed, the density of diamond cluster and the density of diamond grits within each cluster determine how many grits are acting at the grinding zone at the same time. Under controlled force grinding as proposed to be used in the grindability test, these parameters determine the load on individual grit. Therefore, it is very important to evaluate this parameter. They will be evaluated both along the circumferential and wide directions.

C. Variation of diamond grit distribution within an individual cluster

As shown in Figure 8, the surface of a diamond belt consists of arrays of diamond clusters. As discussed above, this density of diamond grit distribution within an individual cluster influences the single grit load during grinding.

Figure 6 Proposed specimen

Figure 7 Schematic illustration of work-belt interaction

Figure 8 Schematic illustration of diamond belt surface

D. Variation of cluster diameter

If the density is the same, bigger clusters contain more diamond grits than smaller ones. Cluster size variations should be also evaluated.

The evaluation of the above-mentioned parameters will be performed at 30 locations with 10 locations in the middle of the belt and 10 locations near each side of the belt. The belt thickness is measured using a micrometer. The cluster diameter will be obtained from the SEM image with a magnification of 100. The cluster density is determined by counting the number of clusters within a predetermined area. The counting will be performed with the aid of a camera as shown in Figure 9. The camera is mounted on a 3-dimensional coordinate measuring machine. The specimen is mounted on a station which is fixed on the base. The image of the cluster is magnified and displayed on a TV monitor. Counting the number of clusters with the camera moving in x-direction for a given distance, and then y-direction for some other distance. The density of diamond grits distribution within an individual cluster will be obtained with the aid of a SEM. This data will be analyzed to find out whether the belt is statistically uniform from location to location. T-test or ANOVA analysis will be used to compare belt characteristics. The analysis and results will be presented in the next report. Experiments will also be conducted for future belts before testing to show that belts from different batches have statistically the same characteristics.

2.3.2 Dynamic Grinding Characterization

A more important aspect of characterizing a belt is from its grinding aspect. Diamond belts with the same geometric characteristics may perform differently during grinding. Therefore, it is necessary to evaluate diamond belts through grinding test. The grindability test procedures can be readily adopted to evaluate belt performance. For this purpose, belts from different batches will be chosen to grind the same ceramic material under the same grinding condition. Volumetric material removal rate, power consumption, belt surface variation and work surface finish will be measured and used as criteria to evaluate grinding performance of a belt.

2.4 Design of the Test Machine

As discussed in section 2.2, controlled force grinding is the most suitable method to test grindability. The test machine will be designed based on this definition.

Theoretically speaking, there are several ways to accomplish this goal. Pneumatic cylinder, hydraulic cylinder, torque control motor and ball screw mechanism, and pulley with weight. Let us now discuss each options. With pneumatic cylinder, load cannot be maintained to a constant value if pressure fluctuation exists in the air line. Also, the availability of pressurized air may impose limitation. If hydraulic cylinder is chosen, a hydraulic system is needed for the test machine which can make the machine complex. One of the limitations of torque control motor is that the torque output varies during one motor revolution. This variation will be more evident when the motor is running at low speeds. In our application, the infeed is very small, especially with hard to grind materials which requires that the motor run at very low speeds. The pulley with weight option should be the simplest and most reliable method.

Figure 9 Illustration of cluster density measurement

Under controlled force grinding, there are two ways to accomplish this goal. With the first option, the specimen is force to the belt under certain load as shown in Figure 10. The grinding continues until the predetermined time limit is reached. The accumulated material removal divided by the time leads to the volumetric material removal rate. With the second option, the grinding continues until a predetermined amount material is removed. Dividing the amount removed by the time spent to remove this material leads to the volumetric removal rate. The problem with the second options is that it may take very long time to grind away the given amount material, which may lead to a significant wear of belt. The belt's grinding performance may vary significantly due to this severe belt wear. In our design, the first option will be used. Level 1 design of the machine has been completed and a schematic sketch of the machine layout is shown in Figure 10.

3 Status of Milestones

See the attached milestone schedule.

4 Communications/Visits/Travel

On November 20, 1993, Natesh Krishnan attended a seminar on ceramics grinding

On January 15, 1994, Changsheng Guo gave a presentation at the Directors' meeting about the updated progress of the project and the definition of grindability as reported above.

5 Problems Encountered

Several belts have been evaluated to determine their suitability for this application. An appropriate belt is yet to be identified.

6 Publications

None.

Figure 10 Illustration of test machine

Appendix
List of Related Literature

- 1 Malkin, S. and J. Ritter, "Grinding Mechanisms and Strength Degradation for Ceramics"
- 2 Konig, W. and Wagemann, A., "Machining of Ceramics Components: Process-Technical Potentials"
- 3 Liang, "Grinding of Ceramic Materials, A Model for Energy Consumption and Force Transformation"
- 4 Sumramanian, K., Redington, P.D. and Ramanath, S., "A System Approach for Grinding of Ceramics"
- 5 Roth, P., and Tonshoff, H.K., "Influence of Microstructure on Grindability of Alumina Ceramics"
- 6 Richerson, D., "Modern Ceramic Engineering"
- 7 Hosokawa, A., Yasui, H. and Higuchi, K., "Influence of Wet Grinding Temperature on Surface Morphology of Fine Ceramics"
- 8 "Engineered Materials Handbook", Vol.4, Ceramics and Glass
- 9 Surface, Cylindrical & Internal Grinding of Ceramics
- 10 Surface Grinding Induced Phase Transformation and Residual Stress in $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Composite
- 11 Effect of Grinding Conditions upon Bending Strength of Alumina Ceramics
- 12 Off-line Optimization of Creep-Feed Grinding of Alumina Ceramics
- 13 Technological Requirements for High Efficiency Deep Grinding
- 14 Kovach, J., "Feasibility Investigation of High Speed Low Damage Grinding for Advanced Ceramics"
- 15 Marinesco, I., "Tribo Technological Aspects of Brittle Materials Grinding"
- 16 Miyahara, E., "A study on Grinding Technology of Silicon Nitride for Application to Automobile Engine Parts"
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- 18 Saurwalt, J., "Development of a Predictive Grinding Model for the High Quality Machining of Engineering Ceramics"
- 19 Moriwaiki, T., Iwata, K. and Okuda, K., "Basic Study on Machinability of Ziconia Ceramics in Precision Diamond Cutting"
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- 25 Uematsu, T, Suzuki, K., Yanase, T. and Nakagawa, T., "A New Complex Grinding Method for Ceramic Materials Combined with Ultrasonic Vibration and Electrodischarge Machining,"
- 26 Tonshoff, H.K., Siemer, H. and Wobker, H.G., "Residual stress Measurements of Ceramic Materials After Grinding"
- 27 Yui, A., Watanabe, T. and Yoshida, Y., "Effects of the Grinding Process upon Surface Grinding Accuracy of Advanced Ceramics"
- 28 Hahn, R.S., "Ceramic Grinding with Self-Sharpening Diamond Wheels"
- 29 Suzuki, K., Uematsu, T. and Nakagawa, T., "Highly Efficient Finishing of Ceramics by Helical Scan Grinding"
- 30 Liao, T.W., Sathyanarayanan, G. and Buehler, W.L., "The Selection of Optimal Parameters for Minimum Damage in Creep-Feed Grinding of Alumina"
- 31 Tonshoff, H.K., Telle, R. and Roth, P., "Chip Formation and Material Removal in Grinding of Ceramics"
- 32 Subramanian, K. and Keat, P.P., "Parametric Study on Grindability of Structural and Electronic Ceramics--Part 1"
- 33 Goulger, F.W., Shaw, H.L. and Johnson, H.E., "Constant-Pressure Lathe Test for Measuring the Machinability of Free-Cutting Steels"

- 34 Date, S.W and Malkin, S., "Effects of Grit Size on Abrasion with Coated Abrasives"
- 35 "Tool-Life Testing with Single-Point Turning Tools," ISO Standard 3685, 1993.
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- 38 Birl, J.D. and Ratterman, E., "An Approximate Ranking of the Sawability of Hard Building Stones Based on Laboratory Tests".
- 39 "Metalworking Reference Manual", 3M Company.
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MILESTONE SCHEDULE

To date

Future

Grinding Optimization for Advanced Ceramics

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Objective/Scope

The overall objective of this project is to develop guidelines and recommendations for grinding optimization of advanced structural ceramics to achieve minimum cost and maximum reliability. The following steps are being taken to achieve the objective: conduct grinding experiments jointly with industrial participants, determine effect of grinding parameters on machining damage and strength, elucidate mechanisms of material removal and damage formation, evaluate several damage detection techniques, and transfer data and information to industry in computerized database format.

Technical Progressa) Background

The goal of the ceramic machining program at NIST is to provide measurement methods, data, and mechanistic information needed by industry to develop innovative cost-effective methods for machining advanced structural ceramics. Research projects are carried out jointly with industry and academic institutions under the auspices of the Ceramic Machining Consortium. In addition to NIST, the consortium currently has seventeen members - Ceradyne, Inc.; Cincinnati Milacron, Inc.; Corning, Inc.; Dow Chemical Company; Eaton Corporation; Eonic, Inc.; Ford Motor Company; General Electric Company; General Motors Corporation; Norton Company; SAC International Ceramics, Ltd.; Stevens Institute of Technology; Texas A&M University; Tower Oil and Technology Company; University of Maryland; W. R. Grace & Company; and West Advanced Ceramics, Inc. Current projects include: 1) Grinding Optimization, 2) Characterization of Machining Damage, 3) Nano-Precision Grinding, 4) Chemomechanical Effects, 5) Grinding Mechanisms, and 6) Machinability Database. Consortium members participate in these projects by providing materials, testing, advice, and other in-kind contributions. Funding for the projects is provided by DOE - Ceramic Technology Project, ARPA - Ceramic Bearing Technology Program, NIST - Ceramics Division, NIST - Office of Intelligent Processing of Materials, and NIST - Standard Reference Data Program. Highlights of the projects that are funded in part by DOE are described below.

b) Introduction

Grinding with diamond wheels is the most prevalent method of machining advanced ceramics. This machining method is highly complex and its optimization requires detailed knowledge of many interdependent factors. The major elements of a grinding system are the grinding wheel, the grinding fluid, the machine tool, and the workpiece. Each of these is associated with several parameters that can influence the grinding process. For example, the type of diamond grit, its size and concentration, as well as the bonding material control the behavior of the grinding wheel. The chemical and physical properties of the grinding fluid, and method of delivery to the grinding zone contribute to the grinding rate and the quality of the finished surface. The variables used in grinding such as feed rate and wheel surface speed, and the machine tool characteristics such as stiffness and vibration are major factors in grinding. The workpiece

material and its properties are important factors in the selection of the grinding parameters since each material responds differently to the grinding action.

Optimization of the grinding process consists of finding the most appropriate set (or sets) of parameters to be used for each material such that a maximum machining rate is obtained and at the same time relevant performance parameters such as strength and/or surface roughness are maintained at the required level. This objective requires data and information on the effect of grinding parameters on material removal rate, strength, surface roughness, surface integrity, residual stress and others. In addition to these data, detailed information on the mechanisms of material removal processes, and reliable methods for damage detection are required.

c) Grinding Optimization

A primary activity of the Ceramic Machining Consortium is the development of grindability data for ceramic materials. The main objective of this activity is to establish the relationship between grinding conditions, surface finish, and strength. A strong emphasis is placed on identifying those grinding conditions which will result in the maximum material removal rate while maintaining a given level of strength and surface roughness. This approach reflects the designers' need to meet strength and surface finish specifications and at the same time achieve the lowest possible costs in manufacturing.

A major effort is currently underway to generate grindability data on three different silicon nitride ceramics. Approximately 3000 specimens are being utilized in this test program. A design of experiments plan has been formulated to insure the statistical validity of the results. Eight consortium members have volunteered to conduct grinding tests to meet the requirements of the plan. Additionally, three members have volunteered to carry out optional tests which will examine certain conditions that lie outside the bounds of the formal test framework.

An outline of the basic experiment is as follows: Prepare flexure test bars according to the procedures and specifications in ASTM Standard C1161-90. The bar dimensions are those prescribed in the ASTM Standard for a B-size bar (3.0 mm thick by 4.0 mm wide by 45+ mm in length). Initially, the bars are ground oversize with a thickness of 3.125 mm to allow for material removal from one face during experimental grinding. That face will be the tensile face in a subsequent flexure test. After completion of experimental grinding according to the prescribed parameters, the remaining chamfers are applied. Four-point flexure tests are carried out to determine the fracture strength of the specimens. Fractographic examinations are conducted to locate and assess the nature of the fracture origins in the bars. Stylus profilometry is then employed to characterize the topography of the experimentally ground surfaces. Finally, a rigorous statistical evaluation of the data is carried out.

Meaningful strength characterization dictates the use of Weibull statistics with the requirement that at least 30 replicate specimens be prepared for each set of grinding conditions. As noted above, approximately 3000 specimens – 1000 specimens of each of three different silicon nitride materials (RBSN, SRBSN, SSN) – will be employed in the test program. At the present time, the required number of specimens have been sliced from fully processed billets and ground to the prescribed oversize dimensions. The specimens have been numbered to identify batch, billet, and location in the billet. To minimize the possible bias associated with variations in specimen properties due to systematic batch-to-batch or other preparation differences, the specimens have been randomly selected for assignment to the participating consortium members.

A set of detailed instructions has been prepared giving procedures for grinder setup, specimen mounting, wheel mounting and dressing, data reporting, as well as providing the assigned grinding conditions to each participant. The instructions, specimens, and a set of two specially

prepared resin-bond diamond-grit grinding wheels (prepared by one of the consortium members under controlled conditions for this project) has been delivered to each of the participating consortium members. Current plans call for the experimental grinding to be completed and the specimens to be returned to NIST by mid-May. At that time the specimens will be sent out for final chamfering and returned to NIST for strength testing, fractography, surface finish measurements, and final statistical data evaluation.

To gain some preliminary information on the grinding behavior of the silicon nitride materials selected for this project, an instrumented surface grinder was used to measure the forces associated with grinding. A three-component piezoelectric force transducer, especially designed for grinding force measurements, was used. A resin bond 320 grit diamond wheel with 100 concentration was used with three different commercial grinding fluids. The grinding fluids consisted of an oil in water emulsion, a semi-synthetic, and a synthetic fluid, designated A, B, and C, respectively. An air bearing spindle was used at a fixed wheel speed of 3600 rpm (2300 m/min surface speed). The down feed ranged from 5 to 127 μm , and the table speed ranged from 1 to 10 m/min. Various combinations of down feeds and table speeds were used to obtain a wide range of conditions. The measured forces were then used to calculate the specific grinding energy, defined as the energy used in removing a unit volume of material from the surface. It was found that the specific grinding energy varies with the grinding parameters and depends on the material type. An example is shown in Figure 1, where the specific grinding energies for the three types of silicon nitride are plotted against the material removal rates per unit width of wheel contact. In a similar experiment with the three commercial grinding fluids, Figure 2, it was found that the specific grinding energy also depends on the type of cutting fluid used during grinding. Therefore, the specific grinding energy is not an intrinsic material

Figure 1. The specific energy of grinding for three silicon nitride materials using a semi-synthetic grinding fluid.

property, since it depends also on the grinding parameters. The following additional conclusions were derived from this work: 1) a smaller 1200 size grit produces a higher grinding force compared to a larger 320 grit; 2) grinding forces are lower for the RBSN material than either of the SSN or SRBSN materials; 3) up grinding produces larger forces than down grinding; and 3) grinding forces increase with larger equivalent chip thicknesses, down feeds, and the material removal rates.

Figure 2. The specific energy of grinding for RBSN using three types of commercial grinding fluids.

b) Machinability Database

The objective of this project is to develop a database containing evaluated machinability data for ceramics for use with personal computers. The *Ceramic Machinability Database* will provide access to machinability data for different types of ceramics and will help users such as manufacturing engineers, tooling managers, and machinists develop machining plans for cost-effective production of ceramic parts. For example, the manufacturing engineer, having selected the appropriate material and machining operations for the part, desires to know what machining parameters to use. The database will provide this information.

The search strategy and the structure of the database have been developed jointly with the NIST Standard Reference Data Program. A commercial database management software was selected and has been used to develop a prototype version of the *Ceramic Machinability Database*. A typical search of the database begins with the user choosing the material of interest and the machining operation. Next, the user may view all of the records corresponding to that material and machining operation, or may further narrow the search by some criteria. For example, the user may wish to look only at records where the surface roughness produced by machining is within a certain range. After all of the search criterion have been entered, the

records that satisfy the search criteria are displayed. The user can change the order of these records, view them one at a time, or see them as a group. The records contain complete machining parameters and results of measurements of strength, surface roughness, and machining forces. The user also can compare the search results graphically. An example of a search screen is shown in Figure 3.

Figure 3. A sample search screen from the *Ceramic Machinability Database*.

c) Characterization of Machining Damage

In general, three types of cracks can be produced in ceramics by grinding: lateral cracks (parallel to the surface), median and radial cracks (perpendicular to the surface), and small intergranular and transgranular microcracks. The objective of this project is to evaluate the feasibility of thermal wave measurement techniques for detecting and characterizing the machining damage in ceramics.

The thermal-wave measurement method is a powerful tool for evaluating the thermal properties of materials. This method is based on the measurement of the temperature distribution (both in time and in space) generated by localized heating of the material being tested. It has the advantages of being non-destructive and non-contact, and can provide information on the thermal properties of the material as a function of depth. In our study, the samples were heated locally by a modulated laser beam. This modulated heating generates a changing temperature distribution, i.e. thermal wave, in the sample and in the air above the sample. The thermal wave in the air causes a modulated change of the index of refraction. The temperature distribution is then detected by measuring the deflection of a probe laser beam passing through the air near to the sample surface. This method is sometimes referred to as the mirage-effect thermal wave

technique; and it is, in principle, sufficiently sensitive to detect surface and near surface microcracks, because the microcracks can change the local thermal flux.

In the work reported here, controlled damage was introduced by Vickers indentation to enable the direct evaluation of the crack detection capabilities of the thermal wave technique. Indentations were performed on soda-lime glass and HIP'ed silicon nitride to produce median, radial and lateral cracks with well-known crack geometries. The indented samples were gold coated and viewed in the SEM, and then analyzed by the thermal wave method. In the measurements of the indented specimens, the radius of the heating beam was $10\text{ }\mu\text{m}$ and that of the probe beam was $15\text{ }\mu\text{m}$. A raster scan of specimens was performed. The received image consisted of a background signal obtained from the material, and peak signals from local temperature rise due to the reflection of thermal waves from a defect, for example, a crack.

Figure 4 (a) shows the indent and pattern of cracks intersecting the surface of the glass specimen. In order to detect the median/radial cracks emanating from the corners of the indent, the transverse component of the deflected probe beam (parallel to the sample surface) was used, since this component detects the thermal waves with preferential propagation along the surface and perpendicular to the vertical crack plane. An image of a raster scan on the specimen is shown in Figure 4 (b), using a step size of $5\text{ }\mu\text{m}$ in both x and y directions. The scan covers a $200\text{ }\mu\text{m} \times 200\text{ }\mu\text{m}$ area, giving approximately the same scale as in Figure 4 (a). The modulation frequency used was 20 Hz, corresponding to a thermal diffusion length of $100\text{ }\mu\text{m}$ in the material. In the image, the darker areas indicate a larger signal corresponding to higher local temperatures in the specimen. In these high temperature regions, the heat flow is disturbed by the existence of a defect or a crack. The Y shape of the vertical cracks can be clearly seen in Figure 4 (b). This indicates that the signal corresponds to the median/radial crack system, but not to the lateral cracks. Also, the signal is unaffected by the depression of the indent. This is expected since the purpose of utilizing the transverse component of the deflected probe beam is to enhance the detection of the vertical surface cracks and to reduce the influence of surface topography. It is important to note that only the vertical cracks located along the probe beam are sensed by this technique. The cracks along the x direction are located in a plane parallel to the heat propagation direction and do not disturb the heat flow, and therefore are not detected.

Figure 4. (a) Schematic drawing of the indentation damage on glass; and (b) thermal wave scan of the surface using the transverse component of the deflected probe beam (the scan area is $200 \times 200\text{ }\mu\text{m}$).

Figure 5 (a) is a schematic drawing of the indentation damage on the silicon nitride specimen showing the indent and a well developed median/radial crack system. Figure 5 (b) is a thermal image using the normal component of the deflected probe beam. The bright spot located in the middle of the image corresponds to the center point of the indent; the surrounding area with different grey scale indicates reflection of the thermal waves from subsurface damage, i. e., the lateral cracks. The vertical cracks are not clearly seen in this image because the normal component of the deflected beam is more sensitive to cracks that are parallel to the surface, i.e., lateral cracks.

Figure 5. (a) Schematic drawing of the indentation damage on silicon nitride; and (b) thermal wave image using the normal component of the deflected probe beam (the scan area is $300 \times 300 \mu\text{m}$).

The following conclusions can be drawn from this work. The mirage-effect thermal wave technique can be used to detect both median/radial and lateral cracks in ceramic materials. By using different components of the deflected probe beam, one of the two crack systems can be enhanced. This feature can be used to distinguish different patterns of defects when an unknown damage is investigated. The transverse component of the deflected probe beam can be used to detect vertical surface-breaking cracks without much influence from the surface topography. When the transverse component is used to detect vertical cracks, the cracks along the probe beam scan direction will not be detected. This feature can be used to detect any defects that result in thermal anisotropy in a material.

Status of Milestones

1. Prepare 300 specimens ground under "best in-house" conditions to establish bounds for a more extensive data program (9/1/92 completed).
2. Complete fracture testing, characterization, and preliminary statistical analysis of data (12/1/92 completed).
3. Evaluate feasibility of thermal wave measurement on selected flexure specimens ground under different conditions (4/1/93 completed).
4. Select grinding conditions based on statistical design of experiments, and distribute additional 2000 flexure bars for grinding (6/1/93 completed).

5. Develop a preliminary database structure to be used for data collected in this study and those collected from literature (9/1/93 completed).
6. Measure grinding forces, and evaluate the effects of down feed, table speed, wheel grit size, and grinding fluid (1/1/94 completed)
7. Characterize fracture strength and surface roughness of 2000 flexure bars prepared with three different silicon nitride materials (4/1/94 delayed until 10/1/94)
8. Compare the results of thermal wave measurement with ultrasonic evaluation of the selected samples ground under different conditions (7/1/94 on schedule)
9. Add the recent data to the database and arrange for testing of the prototype by the consortium members (10/1/94 on schedule)

Publications

1. S. Jahanmir and L. K. Ives, "Machining of Advanced Ceramics," submitted to Tribology International.
2. T. Strakna, S. Jahanmir, R. Allor, and K. Kumar, "Influence of Grinding Direction on Fracture Strength," manuscript in review for ASME Journal of Engineering for Industry.
3. H. S. Ahn, L. Wei, and S. Jahanmir, "Non-destructive Detection of Damage Produced by a Sharp Indenter in Ceramics," manuscript submitted for Symposium on Measurement and Inspection of Products and Processes, ASME Winter Annual Meeting, Chicago, IL, November 13-17, 1994.
4. S. Jahanmir, T. Strakna, G. Quinn, H. Liang, R. Allor, and R. West, "Effect of Grinding on Strength and Surface Integrity of Silicon Nitride, Part 1," International Conference on Machining of Advanced Materials, NIST, Gaithersburg, MD, July 20-22, 1993.
5. S. Jahanmir, T. Strakna, G. Quinn, R. Kopp, S. C. Yoon, and K. Kumar, "Effect of Grinding on Strength and Surface Integrity of Silicon Nitride, Part 2," International Conference on Machining of Advanced Materials, NIST, Gaithersburg, MD, July 20-22, 1993.

Chemically Assisted Machining of Ceramics

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Objective/Scope

The ceramic industry has identified the lack of a rapid low cost ceramic machining technology as one of the major barriers for widespread use of ceramics. Current machining technology for ceramics is slow and labor intensive. Residual surface damage on machined surface and the characterization of such surface defects are the key industrial concerns. This project aims to increase the machining rate of ceramics using chemical reactions at the interface. The chemical reactions could change the hard ceramic surface into something softer hence reduce the contact stresses and damage. The reaction product layer produced could also change the conditions at the interface between the diamond abrasive and the ceramic surface reducing the wear of the diamond thus increasing the machining rate. Si_3N_4 is the main material of focus, but other materials such as SiAlON or SiC will also be examined.

The project involves several subtasks including:

1. Development of a bench test simulation to allow screening of chemistries under well-controlled conditions. Identify new chemistries that can significantly improve the machining rate of ceramics, especially for silicon nitrides.
2. Set up a surface grinder and develop test procedures to test and validate various chemistries identified in the bench test.
3. Characterize the quality of the machined surface. Develop a simple test method that can link surface damage from machining to strength. Establish surface quality using such technique for various chemistries.
4. Establish limits of performance and applicability of the chemistry on different material compositions and processes. Establish optimum machining conditions for each chemistry, material combinations.
5. Validate the concepts and methodology in industrial applications.

Technical Progress**CUTTING TEST**

The cutting data bank suggests that the material removal rate (MRR) is a complex function of the chemistries of the cutting fluid. In a typical cutting operation, the rate deteriorates with time. The initial rates are generally fast and are about the same for most of the fluids tested. A typical rate versus cutting time curve is shown in Figure 1. An effective cutting fluid should maintain the rate of cutting. It is necessary to analyze the data base accumulated so far to see if there are systematic trends related to the molecular structures of the chemicals used.

Figure 1 Characteristic ceramic cutting curve: a high initial rate followed by a slow down due to the possible blocking of diamond grit from the cutting debris.

In machining, several aspects of the machining fluid, from a chemical perspective, are important. Surface tension, molecular weight, dielectric constant, density, chain length, and the molecular structure control the reactivity of the compounds with the surface. However, mechanistically, the fluid has to reach the cutting edge first. Therefore, the spreading coefficient or surface tension of the fluid as modified by the molecular weight of the active structure influences the rate of different chemical compounds reaching the cutting edge. The conditions at the cutting edge generally are severe enough that we can safely assume that the reactions take place instantaneously. From this consideration, a series of correlational studies was conducted to examine various parameters with the cutting rates. Eight chemical compounds were selected for the correlation study. These compounds were selected based on different functional groups, chain lengths, and the availability of property data such as surface tension, dielectric constants, etc.

Figure 2 shows the relationship between surface tension and the material removal rate (MRR). As expected, there is a general correlation between the two parameters. The lower the surface tension, the higher the MRR. This suggests that the ability of the compounds to reach the cutting edge may be important. Oleic acid, water, and hexane seem to deviate a little from the curve but the overall relationship is reasonable. Figure 3 shows the relationship between MRR and the molecular weight of the compounds. Considerable scatter was observed but the general observation suggests that higher the molecular weight, higher the MRR. Of course, within these two figures, the hidden parameter may be the polarity, i.e. the ability of the molecules to adsorb onto the surface. How to define polarity for the compounds, however, is a problem. The dielectric constant of a molecular structure in solution may indicate the relative adsorbability of the structure, hence, polarity. Figure 4 shows the relationship between the MRR and the dielectric constant. The result actually suggests the opposite trend, the higher the dielectric constant, hence higher polarity, the lower the cutting rate. Different combinations of these parameters were attempted. Figure 5 shows the final correlation. Molecular weight, surface tension, dielectric constant and density were included for the best correlation.

The significance of these correlations are difficult to assess at this time. Surface tension and the dielectric constant seem to dominate among the parameters attempted. The molecular weight and the density ratio seems to account for the size effect of the molecules. The basic assumption that the ability of the molecules to reach the cutting edge controls the chemical effects appears to be valid. The validity of this result from the correlation study will need to be verified by a much bigger data base and more accurate estimation of the magnitude of the parameters in solution conditions. Nevertheless, this simple study offers additional insight into the machining process and the role of the chemicals influencing the mechanical processes.

GRINDING TEST

As reported previously, we noticed when we used a candidate fluid, the normal force was unusually high, resulting in a low coefficient of friction on the surface grinder. Several experiments were designed to investigate this phenomena.

I. One Pass Grinding Test

Figure 2 The effect of surface tension to the MRR (material removal rate).

Figure 3 The effect of molecular weight to the MRR (material removal rate).

Figure 4 The effect of dielectric constant to the MRR (material removal rate).

Figure 5

The combined effect of molecular weight, surface tension, dielectric constant and density to the MRR (material removal rate).

The ranking of chemicals on the cutting device is clear-cut. When the same chemicals are tested on the surface grinder, it is difficult to measure the grinding rate and the surface finish after each test. A commercial fluid, 3 % Meqqem in water was used as the baseline. When both fluids were tested on a constant feeding basis, the grinding normal force with the candidate fluid was almost twice as high as the baseline, even though the tangential forces are equivalent. This may be due to several factors: viscosity effect, surface hardness changes, machine deflection, and greater real contact areas. In order to understand the phenomenon and to develop a clear measure of grinding rate, a one pass grinding test procedure was developed. The test procedure is as follows:

- 1) Material: Silicon nitride from CERCOM, the batch number is PSX-HIP117.
- 2) Geometry: 4 Inches long, 1 inch wide and 1/4 inch thick.
- 3) Grinding wheel linear speed: 23 m/s.
- 4) Horizontal feeding speed: about 0.15 m/s.
- 5) Grinding fluid: baseline fluid 3 % meqqem in tap water, candidate 1190 (organic), and candidate 1195 (water-based fluid at 10 % treat rate).
- 6) Dressing: Before each test, the grinding wheel was dressed by the same dressing stone in 3 % meqqem fluid.
- 7) Surface preparation: The spindle of the wheel is a cantilever. Under a given down-feeding, the cantilever may deflect a little. For a single pass grinding, the whole grinding surface must be produced without deflection. Thus, the down-feed was set initially at 0.0127 mm/pass. The purpose is to grind a plane which is parallel to the table. After all of the surface area was ground, the down feed rate was reduced to 0.0076 mm/pass and three passes were conducted. Then, the down feed rate was reduced to 0.0025 mm/pass and ground thrice. Finally, there was no down feeding and the grinding wheel passed the sample without any material removal.
- 8) Down-feed: Moved the grinding wheel at a fixed distance from the sample, set the down feeding equal to 0.025 mm/0.050 mm.
- 9) Single pass grinding: Aligned the wheel at one third of the width, drove the sample to move toward wheel, under the given down-feed, the wheel remove the material to form a groove. After the sample passed through the wheel, the test was stopped.

The results from the three fluids are shown in Figure 6. Their normal and tangential forces are shown from Figures 7 to 9. Candidate OA-1000 which is a superior cutting fluid shows the worst result among the three. It shows the highest normal force. It is this high normal force which we believe that it deflect the grinding wheel from touching the sample.

From the single pass grinding data, it appears that the extraordinary high normal force is

Figure 6 a) The cross-section of single pass grinding sample with 3% Meqqem in tap water. b) The cross-section of single pass grinding sample with OA. c) The cross section of the single pass grinding sample with 5 % 1195 in tap water.

Figure 7 a) The measured grinding forces with 3% Meqqem in tap water under a $25 \mu\text{m}$ down feeding. b) The measured grinding forces under a $50 \mu\text{m}$ down feeding.

Figure 8

a) The measured grinding forces with fluid OA-1000 under a 25 μm down feeding.
b) The measured grinding forces under a 50 μm down feeding.

Figure 9 a) The measured grinding forces with 5% 1195 in tap water under a 25 μm down feeding. b) The measured grinding forces under a 50 μm down feeding.

probably from the hydrodynamic lift from the high fluid viscosity of the organic fluid. The additional lift caused more deflection of the spindle and therefore distorted the machining rate data.

The single pass experiment partially explains the high normal force observed on the surface grinder, but the single pass grinding rate cannot reflect the true performance of the fluids. From the cutting data, the initial rates of cut for most of the fluids are the same, but the steady state rates are very different. Therefore, a single pass grinding cannot be used to evaluate the removal rate for the grinding fluids under a given down feed rate. A constant loading grinding system was needed. This was designed and built.

Constant Loading Single-Pass Grinding

To accurately measure the effects of the chemistry, a constant load grinding test procedure was developed. A force transducer was mounted on the slide-way and a dead weight was applied on the sample-mount with a thick steel cable. The grinding wheel was adjusted to a given overlap. A displacement transducer was fixed at the base to measure the movement of the sample-mount. The material removal rate could be measured continuously by the displacement under a constant load in different environments. The test conditions were listed below.

- 1) Test material: Silicon nitride obtained from Kennametal.
- 2) Geometry of the test samples: 6.35 mm (1/4") wide, 50.8 mm (2") long, 25.4 (1") mm thick.
- 3) Grinding speed: 23 m/s.
- 4) Tangential loads: 22.2 N (5 lbs), 44.5 N (10 lbs), 66.7 N (15 lbs).
- 5) The preset overlap between the sample and grinding wheel surface was 1.016 mm.
- 6) Cutting fluids: 3% meqqem in tap water; candidate fluid OA-1000.
- 7) The normal force and the displacement of the ground sample were measured.

Due to the geometry between the grinding wheel and sample, the grinding wheel gradually cut into the sample. The measured displacement (or distance travelled of the sample-mount on the slide-way) of the ground sample could be used to calculate the material removal rate. The removal rate, R_g , can be written as,

$$R_g = WhV$$

where W is the width of the sample which is equal to 6.35 mm, h is the preset overlap which is equal to 1.016 mm, and V is the speed of the sample movement.

First group of tests was ground with a commercial baseline fluid of 3% meqqem in tap water, the sample was ground with a 22.24 N (5 lbs) tangential load. The normal force as shown in Fig. 10 was about 200 N. The sample was ground for about 30 mm initially then the wheel stopped at that point and could not move any further. A equilibrium between the wheel and the sample had been reached. Unless a higher force was introduced, the sample would not

Figure 10 A constant loading grinding experiment shows the grinding distance and normal force as a function of time. (Test condition: grinding wheel speed 1000 m/s, tangential load 5 lbs, cutting fluid 3% Meqqem in tap water)

be ground further. Post test analysis revealed that the diamond grit were partially worn and the wheel was packed with the debris making the penetration depth shallow.

When the candidate fluid OA-1000 was used, the grinding rate was dramatically increased. The grinding did not stop at the 30mm mark and it proceeded rapidly and finished the whole surface in about 40 seconds under the 22.24 N (5 lbs) tangential load. The normal and tangential forces and the displacement are shown in Fig. 11. These results validated the cutting experimental results. They demonstrated that the chemical effects observed in the simple cutting test were real and could be verified on a surface grinder.

Status of Milestones

On Schedule

Communications/Visits/Travel

Visited Kennametal Inc. on Jan. 11, 1994 to exchange information and discuss the next steps in the cooperation.

Ted Lilley and Patrick Redington of Norton visited NIST on Feb. 8, 1994 to discuss cooperation in ceramic machining

Bob Schulz of DOE visited NIST on Feb. 14, 1994 to review the progress of the project.

John Johnston and Richard Schlosberg of Exxon Research visited NIST on March 29, 1994 to discuss collaborations with respect to surface chemistry detection and analysis.

Problems Encountered

None

Publications

Two to be published.

Figure 11 A constant loading grinding experiment shows the grinding distance and normal force as a function of time. (Test condition: grinding wheel speed 23 m/s, tangential load 5 lbs, cutting fluid 65%OA)

High-Speed, Low-Damage Grinding of Advanced Ceramics

Dr. Joseph A. Kovach (Eaton Manufacturing Technologies Center)

Dr. Stephen Malkin (University of Massachusetts)

Objective/Scope

The fundamental objective of this project is to conduct a feasibility investigation of High Speed Low Damage (HSLD) grinding relative to the development of a single step, roughing/finishing process suitable for producing high quality silicon nitride ceramic parts. Current industrial grinding approaches sacrifice productivity and costs in order to achieve good surface finishes. However, by using high wheel speeds and fine grits to achieve the small grain depths of cut necessary for low damage grinding, it is anticipated that a process can be identified to finish grind silicon nitride at high material removal rates while producing acceptable surface integrity at substantially lower costs than traditional, multi-stage grinding processes.

Technical Progress

This semiannual report summarizes technical progress achieved during the period from October 1, 1993 through March 31, 1994. The report describes activities regarding the University of Massachusetts "Two-Color Detector System" for grinding temperature measurement, as well as Eaton efforts which address potential practical concerns/limitations for the HSLD grinding process. More specifically, during this period, the University of Massachusetts set up the new two-color detector system, calibrated it, and performed initial grinding tests for temperature measurements in a ceramic workpiece. Efforts conducted in the Eaton Machining Research Center (MRC) clearly show the influence of wheel roundness and system balance on the resulting ceramic surface while operating at increased wheel speeds. In addition, technical highlights are provided from a series of HSLD tests designed to increase cutoff rates by creep feed grinding and precision bore finishing rates using alternative I.D. finishing processes.

From a background perspective, it is important to realize that the temperatures generated in the grinding of ceramics may significantly affect the grinding mechanisms and resulting surface integrity. Several Japanese researchers have suggested that elevated grinding zone temperatures may inhibit fracture and promote a non-detrimental ductile mode of grinding. Based on analytical considerations of grinding kinematics, the only practical way to achieve increased grinding zone temperatures while maintaining large removal rates, is through the use of high wheel speeds. However, grinding of ceramics with small grit depths of cut in order to minimize workpiece damage will require high specific energies which, in turn, may lead to higher grinding zone temperatures. In extreme cases, excessive wheel heating could drastically reduce the useful life of the grinding wheel. Therefore, in an effort to optimize this critical heat balance, grinding zone temperatures must be determined.

In order to calculate the temperatures generated by grinding, it is first necessary to know the fraction of the total grinding energy conducted as heat to the workpiece. In the present investigation, an inverse heat transfer method is being used to estimate the energy input to the workpiece from temperature measurements in the subsurface. This energy is then compared with the total measured energy input, obtained from the measured grinding force and power, to determine the fraction of the grinding energy conducted as heat to the workpiece. Two types of temperature measuring systems are being used. The first utilizes a thermocouple embedded in the workpiece. The second utilizes an infrared detector and optical fiber. This latter system is more complex, but should provide much faster temperature response than the embedded thermocouple.

Since the last semi-annual report, additional tests were conducted under straight grinding conditions on Eaton sintered reaction bonded silicon nitride (S/RBSN) using the embedded thermocouple approach. The experimental setup for measuring the temperature response and grinding power is illustrated in Figure 1. Note that a hole is drilled from the under side in each specimen, and then a thermocouple (type K, 36 gauge wire) is installed and held with high temperature cement. The thermocouple junction is initially about 1.2 mm from the top surface of the workpiece. The grinding test is continued by taking successive passes under identical conditions until the thermocouple is ground and destroyed. The machine is then left idle for a few minutes between successive passes in order to ensure that the workpiece returns to ambient temperature before the next grinding pass. The last grinding pass is taken for reference as zero depth, and the locations of the previous grinding passes are then calculated.

Recall that in previous tests the thermocouple response was extremely slow, which rendered the results questionable. In order to improve the response, an attempt was made to reduce the thermal inertia of the thermocouple. A hole with a diameter of 0.75 mm, which is smaller than the one previously used, was drilled in the workpiece such that less cement would be required. However, after several tests the results were still not satisfactory. Based on calculations using moving heat source theory and an analysis of the measured temperature, it was found that the temperature did not rise as rapidly as it should have. Microscopic observations of exposed thermocouple junctions after the tests revealed insufficient bonding of the cement to the surrounding workpiece. The smaller holes made it more difficult to get the cement in the right place. Subsequently, a small amount of solder was used instead of cement to hold the thermocouple in place. Better contact between the thermocouple and ceramic was expected, but the results were again unsatisfactory. Although only a very small amount of solder was used, the thermal inertia of the thermocouple increased significantly causing even a slower response.

From these and previous experiments, it was concluded that temperature measurements using embedded thermocouples are very difficult to control. For the one successful test previously reported, the thermocouple was apparently well seated with cement at the bottom of the hole. Obviously, any future temperature measurements will

Figure 1. Experimental arrangement for grinding temperature measurement.

require a much more reliable system. It is felt that an infrared system, which uses an optical fiber to conduct the signal from the workpiece to a sensor, should be more reliable and also provide much faster response.

The proposed infrared system utilizes a hole from the under side of the workpiece, analogous to the thermocouple system. Radiation from the workpiece is transmitted by a fiber to a detector which converts the radiation energy from the fiber to an electrical signal. To improve system performance a two-color detector, which consists of two photocells (one mounted above the other) has been constructed. The advantage of the two-color detector is that the measured temperature is determined by the ratio of the signals received by two cells, thus the emissivity of the material is not required to evaluate the temperature. It also appears that the conditions on both ends of the fiber may have less influence on the measurement. Furthermore, unlike with a single-color system, movement of the fiber will not affect the two-color system accuracy. It is also expected that the time response of the two-color detector system will be almost as fast as a single detector system.

An InSb/MCT two-color detector was ordered in mid-October from Electro-Optical System, Inc. Although delivery was promised within four weeks, the detector did not arrive until the end of January. The two-color detector system was supplied with built-in preamplifiers and an optical SMA connector in a metal dewar. The unit is operated at a temperature of 77 °K using liquid nitrogen. Two chalcogenide fibers with core diameters of 0.01 and 0.02 inch were purchased. Although a fiber with a larger cross sectional area can transmit more energy, the incident radiation comes from a larger area tends to average the thermal data. A special fixture was also designed and built to hold the workpiece specimen and the optical fiber. Since the fiber is delicate the fixture protects and guides the fiber from the workpiece to prevent fracture if the bending radius becomes too small. This fixture also adapts to a Kistler dynamometer for grinding tests.

For calibrating the system, a blackbody (Figure 2) was made from pure copper to ensure isothermal conditions within the body during cooling. Two thermocouples were installed in the copper body to monitor the temperature. A hole was drilled, threaded and coated with lampblack to provide high emissivity as a true blackbody. A hot plate (Omega, Chromalox Roph-204) with a maximum temperature of 500 °C was purchased to heat the blackbody for calibration. A 240 voltage power line was installed in the laboratory for operating the hot plate. System calibration was performed by monitoring the temperature of the blackbody as it slowly cooled from an initial temperature after heating.

Since the infrared system used in this study employs a fiber to transmit the radiation from the workpiece to the detector, the calibration must be performed with the fiber. As stated above, the two-color detector system consists of two infrared cells, MCT and InSb. The MCT cell has an AC amplifier, and the InSb cell has a DC amplifier. The AC-coupled cell can detect only an AC signal. Therefore, a mechanical chopper was constructed to modulate the radiation from the blackbody so that the chopped signal can be detected by the cell. The experimental setup for calibrating the system is shown in Figure 3, and a chopped signal output in Figure 4. The difference between the highest and lowest values in Figure 4 represents the sensitivity of the cell.

Electrical signals from the two cells are then recorded by a PC data acquisition system. In the initial tests, a fiber with 0.020 inch core diameter was used to calibrate

Figure 2. Calibration Blackbody

Figure 3. Calibration arrangement for two-color detector system.

Figure 4. A chopped signal output from InSb cell at temperature of 380 °C.

the system. Output signals from the two cells are shown in Figure 5. The ratio of the signal from the InSb cell to the signal from the MCT cell versus temperature is shown in Figure 6. Unfortunately, the signal fluctuated and became weaker for temperatures below 200 °C, which greatly reduced the accuracy. After polishing the fiber end, a second calibration was conducted which resulted in more consistent data at lower temperatures. Figure 7 shows the signals after the second calibration, while Figure 8 represents the ratio of the two signals. By comparing the results from these two calibrations, it can be seen that although the absolute values from these two calibrations are somewhat different, the ratios from both of these separate calibrations are very close. It appears that the fiber end condition did not significantly affect the ratio.

Once the system calibration was completed, several grinding tests were conducted on the UMass Brown & Sharpe 1236 Hi-Tech CNC grinder using 8.5 mm wide S/RBSN specimens provided by Eaton. A 12" diameter Norton ASD120-R75B56-1/8 wheel was used at a wheelspeed of 30 m/s and workspeed of 158 mm/s. The wheel depth of cut was 0.0375 mm for grinding with fluid, and 0.0254 mm for grinding without fluid. Prior to grinding, the wheel was trued using a silicon carbide brake-controlled truing device then subsequently conditioned with a silicon carbide abrasive stick. A tape recorder (Racal Recorder/V-store 8) was used to record the signals from the two detector cells, the power monitor, and the Kistler force dynamometer. One channel was used to record voice to facilitate locating data files during signal retrieval. The grinding test involved taking successive passes under the same conditions until reaching the hole with the fiber.

Once having overcome several initial fiber bonding and fluid leakage problems, good strong signal were recorded from both cells. The transient signals shown in Figure 9 were obtained from the two cells at a depth of 0.2 mm below the grinding surface. The maximum signals received from both cells versus depth into the workpiece are given in Figure 10 while the signal ratio is presented in Figure 11. Note that the ratio at shallow depths exceeded the maximum calibration value at 500 °C, indicating that the temperatures exceeded 500 °C. It should be noted that during the last few passes the signals from the MCT cell started to fluctuate. This fluctuation could be caused by degradation of the heated end of the fiber.

The results of these initial grinding tests indicate that the infrared detector can be used to measure temperatures in the workpiece subsurface during the grinding of ceramics. In order to improve performance, subsequent efforts will focus on methods to prevent grinding fluid from contaminating the fiber end. Fibers with smaller core diameters will also be used to detect more localized temperatures on smaller areas of the workpiece. Thermal analyses will be conducted based on the experimental results using moving heat source theory to estimate the energy partition to the workpiece.

In addition to the fundamental temperature measurement testing discussed above, numerous tests were performed in the Eaton Machining Research Center (MRC) to address potential concerns/limitations associated with the HSLD grinding process. Technical highlights are provided from a series of HSLD tests designed to increase cutoff rates by creep feed grinding and precision bore finishing rates using alternative single stroke honing processes. In addition, the Eaton efforts clearly show the influence of wheel roundness and system balance on the resulting ceramic surface while operating at increased wheel speeds.

Figure 5. Signals from InSb and MCT cells from first calibration.

Figure 6. Ratio of signals from InSb and MCT cells versus temperature from first calibration.

Figure 7. Signals from InSb and MCT cells from second calibration.

Figure 8. Ratio of signals from InSb and MCT versus temperature from second calibration.

Figure 9. Transient signals from two cells versus time.

Figure 10. Maximum signal rise from two cells versus depth into the workpiece.

Figure 11. Ratio of two signals (InSb/MCT) versus depth into the workpiece.

In the finishing of structural ceramics, parting operations (i.e. cutoff) are often required to achieve correct component length. From a fundamental perspective, this process is somewhat analogous to surface creep feed grinding. Accordingly, the initial Eaton test series was focused on HSLD cutoff operations using creep feed grinding. The primary objective was to identify potential process limitations with respect to material removal rate and resulting surface finish. During this study, approximately 30 S/RBSN specimens were "slit" lengthwise under full-depth, creep feed grinding conditions using 0.0625" wide wheels. The rectangular specimens, provided by Coors Golden Technologies, were approximately 4.0 " long x 0.370" wide x 0.430" deep.

A schematic representation of the test setup is shown in Figure 12. Note that the specimen is mounted to the "fixture base" by using a cyanoacrylate adhesive. Upon conclusion of the test, the resulting halves are dis-mounted by using either a hot plate (to melt the glue) or a solvent (to soften the glue). In all cases, the fixture base is mounted to a Kistler 3-axis dynamometer to measure forces. In addition, a spindle power monitor was used to help determine the "effective" tangential & normal forces developed under full-depth creep feed grinding conditions. To accurately determine the actual grinding power and forces developed during deep slitting operations, it is important to subtract the forces arising from fluid impact, frictional rubbing on the sides of the wheel, as well as any hydrodynamic forces arising from coolant in the slot. This is done by performing several "dead" passes to characterize the parasitic loss components. During these tests approximately 0.75 H.P. (3 lbs. horizontal force) was consumed by the parasitic losses, which can account for about 25% of the total power.

It is also important to realize that under full-depth creep feed grinding conditions the forces measured by the dynamometer (horizontal and vertical forces) are **not** equivalent to the actual tangential and normal forces. As shown in Figure 13, the horizontal and vertical force vectors must be resolved to determine the total tangential and normal forces which effectively act at the location given by the angle γ . (Since all tests were conducted in the "up" grinding direction, the force vectors shown in Figure 13 apply to up grinding.) In these tests the depth of cut in these tests was quite large (0.430"), consequently the angle γ was also quite large (approx. 16°). Note that the angle γ can be determined by equating the measured power with the measured horizontal and vertical forces. Alternatively, by assuming a triangular force distribution, it can be shown that γ acts at a point approximately 2/3 of the way up the arc-length-of-contact (see "Matching Forces and Power in Creep-Feed Grinding" by Guo, Krishnan, and Malkin, presented at the 5th International Grinding Conference, 1993.). Interestingly, the 2/3 approximation was good to within 2% for the majority of these creep-feed ceramic grinding tests.

As an initial starting point, a Norton resin bonded diamond wheel (SD100 - R 50 B 69, 8" O.D.) was utilized at a feed rate of 0.5 in/minute at full depth (0.430") and a wheel speed of 10,000 SFM. Once the wheel reached the full arc-length-of-cut (approximately 2.25" into the cut), the power spiked dramatically, which in turn actually set the resin wheel on fire. This power spiking phenomenon, known as "burn-out", is commonly observed in full-depth creep feed grinding of metallic alloys, and can be attributed to boiling of the coolant within the workzone. In an attempt to reduce "burn-out", the feed rate was reduced by a factor of two (now at 0.25 in/min). However, once again, the power spiked which also ignited the resin bond in the wheel. Specific energy ranged

FORCE DIRECTIONS

COOLANT CHANNEL

FIXTURED BAR

CERAMIC BAR SLITTING

Figure 12

from 51×10^6 in-lbs/in³ to 154×10^6 in-lbs/in³ (see Table 1).

To improve the initial cutting effectiveness, the wheel was pre-conditioned by taking a series of 36 up-grinding passes through a 5" long 37 C 150 H11 VKPM abrasive stick. A feed rate of 10 in/min was used at a depth of 0.300". Wheel speed remained constant at 10,000 SFM. Just as in the case of the grinding tests, Cimperial 1011 (as a 10:1 ratio) was applied through two nozzles at 40 PSI and 7.5 GPM per nozzle. This conditioning approach was used for the balance of the tests.

Once having re-conditioned the wheel, the test was repeated. Both the specific energy and heat flux dropped considerably. Moreover, burn-out was not observed. However, wheel wear was a concern with the resin bonded wheel. Therefore, in an effort to improve G-Ratios, the wheel was changed to a Regal metal bonded wheel (MD 80 N 50 M).

Using the Regal MD 80 N 50 M wheel, the feed rate was increased until "burn-out" occurred. As shown in Figure 14 the tangential force develops considerable spiking when the fluid begins to boil in the workzone. A similar burn-out spiking behavior was observed for the power and normal force. Note, however, that after burn-out occurs the forces and power return to a value lower than before the spike. Since the power and forces reach extremely high values during the spike, the wheel can self-sharpen (i.e. high forces breakdown the wheel to expose fresh cutting edges). Alternatively, due to the extreme heat, slight expansion of the wheel and/or workpiece can occur to momentarily increase the amount of stock removed, after which time the effective stock removal is temporarily reduced when the wheel/workpiece return to their normal dimensions. The net effect in either case is a subsequent reduction in force.

It should be noted that during spiking (burn-out) an orange fire-band temporarily developed around the periphery of the metal bonded wheel. However, unlike the resin wheel, the metal wheel did not catch on fire. In addition, the burn-out heat flux (140,186 in-lb/ in²-sec) was considerably higher for the metal wheel than for the resin wheel (81,161 to 120,132 in-lb/ in²-sec). Therefore, it was decided to continue to use the metal bonded wheel owing to its higher temperature capabilities and potential for higher material removal rates.

In an attempt to further reduce the propensity for burn-out at increased feed rates, a coolant induction channel was added to the setup (see Figure 12) to assist in directing coolant into the workzone. By introducing additional coolant into the workzone, additional heat energy can be convected away before any vapor barrier forms from fluid boiling. Ideally, a transition from pool boiling to forced flow boiling can be developed in the workzone to increase heat transfer. As Table 1 indicates, by adding the coolant channel, burn-out was eliminated with the metal wheel at the 0.6 in/min feed rate. Subsequently, the feed rate was increased to 1.0 in/min. Again, burn-out was not observed. Note, however, the maximum heat flux did not exceed 125,863 in-lb/ in²-sec. Consequently, it appears that the threshold burn-out heat flux appears to be on the order of 140,186 in-lb/ in²-sec for the MD 80 N 50 M metal bonded wheel. To date, feed rates have been increased to 2.0 in/min at full depth.

In addition to addressing the challenges associated with creep feed grinding, the complexities of creating an I.D. of precise dimension, form and surface finish were also investigated. Initially, tests at Eaton's Manufacturing Technologies Center (MTC) examined the possibility of increasing material removal rates by HSLD I.D. grinding. It

Forces and Power at Burnout or Maximum Grinding Values at Full Depth of Cut (No Burnout)

Test Number	Wheel Type	Coolant Application	Wheel Speed (ft/min)	Part Speed (in/min)	Depth of Cut (in)	Horizontal Force (lbs)	Vertical Force (lbs)	Power (hp)	Specific Energy From Power (in-lb/cu in)	Heat Flux From Power (in-lb/sq in-sec)
1	Resin	No Channel	10,000	0.5	0.437	19.6	47.0	1.8	51,035,973	99,401 B
2	Resin	No Channel	10,000	0.25	0.422	34.0	82.0	2.6	153,745,592	147,130 B
3	Resin	No Channel	10,000	0.25	0.437	21.0	58.0	0.8	46,396,339	45,182
4	Metal	No Channel	10,000	0.6	0.437	31.6	85.0	3.0	73,460,870	153,567 B
5	Metal	Channel	10,000	0.6	0.437	23.0	62.0	1.4	32,864,073	68,701
6	Metal	Channel	10,000	1.0	0.434	30.0	64.0	2.7	39,709,493	137,876
7	Metal	No Channel	10,000	1.0	0.427	14.0	28.0	1.1	16,619,016	57,236 B
8	Metal - Dull	Channel	10,000	1.0	0.425	35.0	100.0	2.2	33,394,447	114,741 B
9	Metal	Channel	10,000	1.25	0.433	31.0	66.0	2.6	29,967,963	129,915
10	Metal	Channel	10,000	1.5	0.435	28.0	32.0	2.6	24,858,483	129,616 B
11	Metal	Channel	10,000	1.75	0.428	22.0	40.0	2.4	20,302,270	122,505 B
12	Metal	Channel	10,000	2.0	0.432	20.0	30.0	2.2	16,426,667	113,807 B

Diamond Slicing Wheel Specifications

Norton Resin Bond 8in O.D. x 0.0625in wide
(100 Grit) SD 100 - R 50 B 69 - 1/4

Regal Metal Bond 10in O.D. x 0.0625in wide
(80 Grit) MD 80 N 50 M - 1/4

Note: "B" after Heat FLux value designates Burnout .

Table 1

Tangential Force vs. Time S/RBSN Bar Slicing

Slicing Conditions

Wheel Type: 80 Grit Metal Bond Diamond Wheel (0.0625 in wide)

Wheel Speed: 10,000 ft/min

Part Speed: 0.6 in/min

Depth of Grind: 0.437 in

Coolant Application: Entrance/Exit Nozzles only

Figure 14

must be realized, however, that conventional I.D. grinding suffers from several limitations. First of all, even with a spindle speed of 60,000 RPM it is difficult to exceed 7800 SFM on small diameter I.D. wheels (e.g. 0.5"). Secondly, the I.D. grinding quill is not very rigid which, in turn, seriously limits material rates. Lastly, due to the "flexible" quill, precision dressing of the diamond I.D. wheel is severely hampered. As a consequence of these factors acting in concert, the resulting bore surface exhibited extreme taper (0.005") even at relatively low material removal rates.

Consequently, the possibility of using a single stroke diamond honing process as a substitute for I.D. grinding was investigated. In these tests all honing was done on a Maho MH-700-S five axis CNC machining center using the horizontal spindle. The objective was to generate an ID to ± 0.0002 in (± 0.005 mm), with a roundness tolerance of 0.000118 in (0.003 mm) and have a surface finish better than 8 μ inches R_a (0.2 micron). Two materials were used for the study, Eaton S/RBSN and Kyocera SN-220. Diamond sleeves, used to produce the ID's, ranged in grit sizes from 100, for roughing, to 1200 for superfinishing.

The tool consisted of a tool holder, mandrel, abrasive sleeve, pilot and adjustment screw. The majority of the tool components were purchased from Sunnen Products in St. Louis, MO. The size of the tool could be set by turning the adjustment screw one indicating notch for every 0.0001 in (0.0025 mm) of stock off the diameter to be removed. The adjustment screw draws the sleeve up the tapered mandrel, causing the sleeve to expand.

All tests were conducted using RD2 265M coolant from Master Chemical of Perrysburg, OH, mixed at a 20:1 dilution ratio. Coolant was applied using a "through the tool" technique and an external flood. Coolant was fed along the shaft from jets 90 degrees apart at the end of the tool holder. The external flood was applied 180 degrees apart. This allowed a direct flow of coolant into the work zone. A feed rate of 30 in/min (12.7 mm/sec) was used to feed the tool through the part. The tool was retracted at 472 in/min (200 mm/sec). The surface speed of the sleeve at 125 ft/min (0.64 m/s).

Two methods of material removal were tried. The first was a fixed stage approach. In other words, the total stock removal would occur over a predetermined number of passes, from roughing to finishing. The number of stages (passes) was determined as a function of the stock envelope and the recommended depths of cut. For the Eaton parts, with an average stock envelope of 0.027 in (0.70 mm), eleven stages were required. Only nine stages were needed to remove the 0.018 in (0.47 mm) stock envelope on the Kyocera material.

Abrasive Sleeve Descriptions

Tool Type	Grit Size	Material Removal Range - Off Diameter	
		(inches)	(millimeters)
Roughing	100	0.001 - 0.004	0.03 - 0.10
Semi-Roughing	220	0.0005 - 0.003	0.013 - 0.076
Semi-Finishing	400	0.00005 - 0.0005	0.001 - 0.013
Finishing	800	0.000025 - 0.0002	0.0006 - 0.051
Super-Finishing	1200	0.000025 - 0.00005	0.0006 - 0.0013

The material removal rate (MRR) was determined by assuming that a cylinder of material was being removed per unit time per unit abrasive width (i.e. length of hone). The length of the sleeve was six inches (150 mm) and the duration of the grind was 0.20 min (**12 seconds**). It should be realized that since the I.D. honing tools are approximately 12 times longer than typical I.D. wheels, the calculated MRR appears rather low. Nevertheless, in a production setting, this process lends itself to low-cost multi-spindle machines. Cycle times on the order of 12 seconds can be expected, versus 2 minutes with traditional I.D. grinding. The table on the following page lists the maximum material removal rate for a given depth of cut.

Material Removal Rates

<u>Depth of Cut Off Diameter</u>		<u>Max. Material Removal Rate at Depth of Cut</u>	
<u>(inch)</u>	<u>(mm)</u>	<u>(in³/in/min)</u>	<u>(mm³/mm/sec)</u>
0.004	0.10	0.0032	0.034
0.003	0.08	0.0024	0.026
0.0005	0.013	0.00041	0.0044
0.0003	0.008	0.00025	0.0027
0.0002	0.005	0.00017	0.0018
0.0001	0.003	0.000066	0.00071

Initially, this fixed stage approach appeared desirable since it could easily be transformed into a production process. The number of machines, cycle times, and other production variables could all be clearly identified. Unfortunately, the parts have to be near final size. If a part has a large stock envelope, large depths of cut are required. In our tests, this method proved unsatisfactory due to excessive chipping at the exit end of the bore. The relatively large depths of cut, 0.003 - 0.004 in (0.08 - 0.10 mm) off the diameter, caused unacceptable chipping. It was shown that the Eaton S/RBSN material had more pronounced chipping than did the Kyocera SN -220 material.

Subsequently, a fixed material removal approach was used with less abusive depths of cut. Roughing was initially tried at 0.001 in. (0.025 mm) off the diameter. Although this approach reduced the exit chipping, deep scratches were developed in the workpiece surface. Based on visual examination, it appeared as though the scratches were more pronounced in the Kyocera material than in the Eaton material. This may be due to the fact that the Eaton material is more porous than the Kyocera material, thus "masking" the apparent scratch depth.

In the next set of tests, the roughing depth of cut was changed to 0.0005 in (0.013 mm) per pass, with finishing at 0.0002 in (0.005 mm) and superfinishing at 0.00005 in (0.001 mm) per pass. Chipping was significantly reduced on the Eaton material, to the point where it could be removed by light surface grinding the chipped face. Unfortunately, the main problem with this fixed material removal approach is the extreme number of steps required to finish the bore. Including all passes for grinding and tool sizing, a total of 45 steps was required to finish the bores.

Little appreciable wear of the abrasive sleeves was observed, with the exception of the 400 grit sleeve. Power increased from the indistinguishable level in the early tests, to approximately 0.12 HP (0.089 kW). Another indication of tool wear was an improvement in surface finish. With a new 400 grit sleeve, the best attainable R_a was 8 μ inch (0.2 micron). After 0.0476 in³ of combined Eaton S/RBSN and Kyocera SN-220 stock removal with the 400 grit sleeve, the R_a improved to 3.4 μ inch (0.09 micron). Based on the observed honing tool wear, this translates to an approximate G-Ratio of over 6000.

From a roundness tolerance perspective, the objective was to develop bore roundness on the order of 118 μ inches (3.0 microns) with a surface finish of 7.9 μ inches (0.2 microns). Measurements were made at the entrance, middle, and exit of the bore. Roundness was worst at the entrance, but in all cases was well within the desired roundness tolerance limits as given in the table below.

Average Roundness at the Entrance, Middle and Exit of Bore

<u>Units</u>	<u>Entrance</u>	<u>Middle</u>	<u>Exit</u>
μ inch	65.4	19.7	33.5
micron	1.66	0.50	0.85

In general, the single stroke honing process was able to create parts that exceeded typical ceramic journal bore tolerances and surface finishes. Some investigation must continue, however, to determine why the entrances of the bores were more likely to be out of round, while the middle of the bore was six times better (on average) than the required bore roundness tolerance. One possibility is due to runout of the tool (the mandrel ranout about 0.002" at the tip). Also, improved material removal rates and optimal abrasive surface feeds need to be determined. Perhaps by lowering the unit grit load (by increasing surface speed), chipping and light scratching can be eliminated. It should also be noted that although the G-Ratios were quite good at conventional honing speeds, the process economics may not compare favorably with I.D. grinding when considering the relatively high honing tooling costs. Additional economic studies are planned for the Phase II follow-on effort.

In addition to the operations discussed above, considerable testing was performed at Eaton MTC to address potential practical HSLD concerns and to better understand the influence of wheel roundness and system balance on the resulting ceramic surface while operating at increased wheel speeds. As given in Figure 15, the relative performance of two similarly manufactured 120 grit brazed diamond wheels is compared. The new 1.0" wheel was to be used in an upcoming series of HSLD G-Ratio studies. Unfortunately, a 15 to 20 pound normal force oscillation was present with the 1.0" wheel versus only a 3 pound oscillation with the 0.5" wheel (see Fig. 15). Indicator ring measurements showed that the wheel was mounted concentric to within ± 0.0005 ". However, by expanding the time scale on the force output trace, it could be seen that the wheel had two high and two low spots on its outside diameter. The force traces presented in Figure 16 represent two revolutions of the 1.0" grinding wheel. Subsequently, measurements taken around the outside diameter of the wheel showed it to be out-of-round by approximately 0.002 inch.

Effect of Wheel Out of Round on Normal Force

Test run with 0.5 in wide
120 grit brazed wheel

Test run with 1.0 in wide
120 grit brazed wheel.

$V_w = 50 \text{ in/min}$ (21 mm/sec)
 $Q'w = 0.125 \text{ sq in/min}$ (1.34 sq mm/sec)
 $V_s = 5,000 \text{ ft/min}$ (25 m/sec)

$d = 0.0025 \text{ in}$ (0.064 mm)
 $b = 0.357 \text{ in}$ (9.1 mm)
 $D_s = 12 \text{ in}$ (305 mm)

Figure 15

Amplitude of Normal Force Hitting on Two High Spots

Wheel As Received

$Q'w = 0.125 \text{ sq in/min}$
 $Q'w = 0.134 \text{ sq mm/sec}$

$Vw = 50 \text{ in/min}$
 $Vs = 5,000 \text{ ft/min}$

After Wearing Down
High Spots [8 cu in
(131 cu cm) material
removed]

$Q'w = 0.075 \text{ sq in/min}$
 $Q'w = 0.81 \text{ sq mm/sec}$

(21 mm/sec)
 (25 m/sec)

After Re-Brazing

$Q'w = 0.125 \text{ sq in/min}$
 $Q'w = 0.134 \text{ sq mm/sec}$

$b = 0.357 \text{ in } (9.1 \text{ mm})$
 $Ds = 12 \text{ in } (305 \text{ mm})$

Figure 16

In an attempt to "round-up" the wheel, approximately 8 in³ of S/RBSN was ground from a series of prismatic specimens. However, as shown in Figure 11, this approach essentially **doubled** the apparent force fluctuation in addition to doubling the total grinding force. As a result, the wheel was sent back to the vendor to be stripped, re-ground, and re-brazed with new abrasive. Upon receipt of the re-brazed wheel, the test was repeated. Again, however, the force fluctuation was still present (see Fig. 16). The exact reason for the out-of-round condition was not determined, but was most likely linked to the high temperature brazing process which could have led to thermal distortion of the unique hub on the 1.0" wheel. Currently, a conventional diamond plating process is being used to recoat the wheel. This new plated 1.0" wheel will then be employed in the HSLD G-Ratio studies in the Phase II follow-on effort.

One of the final series of tests conducted during this semi-annual reporting period involve the generation of precision O.D. tolerances under HSLD conditions. Recall that in previous testing, the majority of the work took place using plated wheels. In this series of HSLD O.D. grinding tests a 400 grit, 100 concentration, resin bonded wheel from Coors was used to grind cylindrical roller specimens made by Eaton and Kyocera. All tests were performed on an instrumented Weldon 1632 grinder. Both normal force and grinding power were measured. A summary of the test conditions and results are presented in Table 2. Unlike in previous tests with plated wheels, the wheel speed was limited to 15000 SFM to avoid de-laminating the resin bonded material from the aluminum core as well as to minimize the possibility of igniting the resin at high speeds.

The resulting normal force and grinding power as a function of wheel speed for the Eaton specimens is shown in Figure 17A and 17B. Note that the grinding power remained relatively constant (see Figure 17B) over the speed range tested; thus indicating that the tangential force decreased with increasing wheel speed. This behavior is typical of what was previously observed with plated wheels¹. Conversely, increasing the wheel speed tended to *increase* the normal force in all tests using this fine grit resin bonded wheel, which is somewhat contrary to what was observed in the previous plated wheel tests¹. Recall that with either 120 grit or 400 grit plated wheels the normal forces were reduced at higher wheel speeds. It is speculated that increasing the wheel speed increased the grinding zone temperatures, thereby softening the resin bond to the point where the abrasive was not rigidly supported and could not readily penetrate the ceramic. Consequently, perhaps only high temperature bond systems (such as vitrified, metal, etc.) should be considered for HSLD grinding processes. Future work will include thermal measurements and various bond systems to better understand this unique normal force behavior at high speeds.

Some indication of resulting surface quality is given Figures 18A & B. Note that in almost all cases, the resulting surface finish and component roundness tended to deteriorate with increased wheel speeds. For comparison, in previous plated wheel tests¹ utilizing 120 & 400 grit abrasive, the surface finish tended to improve with increased wheel speeds using the 120 grit plated wheel, while increasing speeds with the 400 grit wheel resulted in a poorer surface finish. In future studies, tests with a coarse 120 grit resin wheel should be conducted to better understand these potentially opposing tendencies.

Nevertheless, it is important to realize that in generating a high quality surface finish, several additional factors, aside from grit size, must be considered collectively.

Test 94-3 HSLD OD Grinding

Test Number	Roller Type	Roller Number	Wheel Speed (ft/min)	Part Speed (ft/min)	In-Feed Rate (in/rev)	Material Removal Rate (sq in/min)	Normal Force (lbs)	Power (HP)	Surface Finish Ra (micro in)	Roundness (micro in)	Specific Energy (in-lb/cu in)
1	Eaton	E-12	6,500	267	0.000016	0.051	14.3	0.31	10.0	30.7	2,569,327
2	Eaton	E-13	15,000	267	0.000016	0.051	17.5	0.30	24.7	107.3	2,544,220
3	Eaton	E-20	6,500	267	0.000046	0.150	13.5	0.80	9.2	50.4	2,328,805
4	Eaton	E-26	15,000	267	0.000046	0.150	27.5	0.94	16.5	49.2	2,747,990
5	Kyocera	K-4	6,500	267	0.000016	0.051	13.0	0.41	7.4	41.1	3,431,349
6	Kyocera	K-13	15,000	267	0.000016	0.051	18.5	0.21	12.7	46.3	1,740,782
7	Kyocera	K-20	6,500	267	0.000046	0.150	16.3	1.01	7.5	42.7	2,925,561
8	Kyocera	K-24	15,000	267	0.000046	0.150	26.0	1.15	14.5	64.0	3,353,479

Table 2 - HSLD OD Grinding Summary Data with Coors Resin Bonded Wheel

Figure 17A

Figure 17B

Figure 18A

Figure 18B

For example, as alluded to in Figures 15 & 16, any wheel runout can have a profound effect on force fluctuation. This effect can be manifested in reduced surface quality. Additionally, any wheel imbalance can also deteriorate surface finish. More allusive however, is the problem of regenerative chatter which encompasses system compliance, dynamics of the grinding action, as well as all of the previously mentioned factors.

Figure 19 shows the development of some regenerative chatter by going from a wheel speed of 6500 SFM to 15,000 SFM with the 400 grit resin bonded wheel. The amplitude and frequency of the "lobbing" is provided in Figure 20. Note that at low speeds a small 3 lobed pattern is apparent with lobe heights of 0.187 microns. However, as the wheel speed is increased to 15,000 SFM, a pronounced 22 lobe pattern is generated with lobe heights of 0.702 microns.

Typically, the first source of chatter to be considered is wheel imbalance and runout. However, with a dressable resin wheel, runout was negligible. Similarly, wheel balance checks showed the system to be well within accepted levels. Recall, however, that as the wheel speed was increased the normal forces increased (see Table 2 and Figure 17A) which in turn could have contributed to vibration of the workpiece mounting arbor. In addition, it is hypothesized that increasing the wheel speed also increased the grinding zone temperatures to the point where the resin bond could not adequately support the abrasive, thereby resulting in more of a "smearing or stick/slip" cutting action rather than a smooth grinding action. From this perspective, perhaps only *dressable* high temperature bond systems (such as vitrified, metal, etc.) should be considered for HSLD grinding processes.

Status of Milestones

As of April 18, 1994 all milestones have been completed with the exception of milestone #153203 (laboratory grinding studies). To complete the remaining test, as well as the final report, a no-cost extension has been granted through May 31, 1994.

Publications

A paper entitled "A Feasibility Investigation of High Speed, Low Damage Grinding for Advanced Ceramics" was assembled and presented at the Fifth International Grinding Conference held October 26-28, 1993 in Cincinnati and also for the SAE CCM meeting held in Detroit (October 18 - 21, 1993).

References

1. Kovach, J.A. , Blau, P.J., et al., "A Feasibility Investigation of High Speed, Low Damage Grinding for Advanced Ceramics", SME Fifth International Grinding Conference, held in Cincinnati, October 26-28, 1993.

HSLD OD Grinding with Resin Wheel

Workpiece Chatter as Influenced by Wheel Speed

Wheel Speed = 6,500 ft/min

Wheel Speed = 15,000 ft/min

Wheel = Coors 400 grit diamond resin bond (DN 400 R 100 B - 1/8)
Workpiece speed = 267 ft/min
Infeed = 0.000 016 in/rev

Figure 19

HSLD OD Grinding with Resin Wheel

Workpiece Chatter as Influenced by Wheel Speed

Wheel Speed = 6,500 ft/min

Wheel Speed = 15,000 ft/min

Wheel = Coors 400 grit diamond resin bond (DN 400 R 100 B - 1/8)

Workpiece speed = 267 ft/min

Infeed = 0.000 016 in/rev

Figure 20

Laser Scatter Methods for Detection of Subsurface Machining Damage in Ceramics – J. Scott Steckenrider, William A. Ellingson, George A. Forster (Argonne National Laboratory), Michael H. Haselkorn, Charles J. Anderson (Caterpillar Inc.)

Objective/scope

The primary objective of this program is to develop a laser scattering procedure that would provide a direct (near-real-time) indication of changes in the subsurface (and surface) during machining. These changes include both machining-induced damage (such as median crack formation) and surface roughness. A second objective is to evaluate dye penetrant technology as an off-line indicator for surface-breaking crack detection. The laser program is being executed in three steps. The first step is evaluating optimization of the laser scattering procedure to examine specimens machined by innovative techniques. The second step will involve correlation of the laser scattering results with mechanical properties in "real" machined ceramic specimens. The final step will be to develop a prototype instrument to be evaluated for on-line implementation in a production environment. The investigation into dye penetrants for surface defect detection is being conducted in three steps: review of literature, off-site visits to appropriate current users (e.g., Norton) and vendors (e.g., Sherwin, Inc.), and laboratory experiments.

Technical progress

The crack detection work accomplished during this period involved laser scatter and dye penetrants. In laser scatter, three primary achievements were made. First, numerous Si_3N_4 samples were obtained (including those of specific interest in this work, SiAlON and GS44) and analyzed to determine their optical transmission properties at the wavelength of interest ($0.6328 \mu\text{m}$). Second, translation stages, image acquisition hardware, and computer interface hardware were installed to allow automated computer-controlled data acquisition. In addition, a first-version software program was developed to permit 2-D scanning of known regular surfaces. Finally, preliminary 2-D scans were performed on calibration step-wedge specimens to simulate the light-crack interaction.

The second area of crack-detection this period was dye penetrant analysis. First, an initial literature review was conducted to determine the current state of the art in dye penetrant inspection with regard to ceramic materials. In conjunction with this search, ceramic manufacturers were contacted to determine the techniques currently employed on a regular basis. Finally, a comparison of three promising penetrant techniques was made on a thermally shocked SiAlON component known to contain cracks.

Part 1: Laser Scatter

A. Optical properties determination.

Initial procedures and protocols were established to determine optical transmission properties of the Si_3N_4 specimens. Using an integrating sphere and calibrated step-wedges of each material (with step thicknesses ranging from 50 to $800 \mu\text{m}$), we were able to measure total reflection and transmission (including all scattered light) for various thicknesses. This procedure requires a specimen $3 \times 4 \times 50 \text{ mm}$ or larger, and such a specimen was obtained for each of the materials of interest in this program, SiAlON and GS44 (which Caterpillar has used to replace GN10 because of the high cost of GN10). Samples of other available Si_3N_4 materials have been prepared and analyzed as well, and these results are illustrated in Fig. 1. As shown, there is a wide distribution of optical transmission properties among the various Si_3N_4 types. Sensitivity to subsurface lateral (and perhaps median) cracks, whose signal strength is dependent on the amount of light reaching the crack, and hence the depth of that crack, will therefore be highly dependent on the material used.

Figure 1. Measured optical transmission properties for several Si_3N_4 materials. Lines are best fits to optical transmission $T = I_t / I_i = e^{-\alpha t}$, where t is thickness.

B. 2-D laser scatter scans for lateral crack detection.

Because of the highly localized nature of the critical defects of interest in this program, the one-dimensional scanning method used for overall optical transmission characterization is not sufficient. To fully examine a given component's subsurface area, a 2-D scan is required. An automated data acquisition system (including translation stages, communication hardware, and image acquisition hardware) was therefore assembled. The necessary software development for computer control of said system was also completed. While optimization of the automated system, illustrated in Fig. 2, is a continuing process, initial 2-D data scans of the calibration step-wedges (GS-44, SiAlON, and NT164) have been made. Figure 3 shows the experimental arrangement, in which the step-wedge is scanned in the X and Y directions, with scatter data taken every 200 μm . The current system records the full 2-D optical Fourier transform of subsurface (or surface) back-scattered laser light (including spatial frequencies up to $0.2 \mu\text{m}^{-1}$) and computes the average magnitude of all such frequencies. This average Fourier magnitude is then mapped as a function of specimen position, resulting in scatter "images" of the subsurface.

The resulting "magnitude" images for the step-wedge of each material, shown in Fig. 4, indicate the degree of interaction between scattered laser light and subsurface ceramic/air interfaces (i.e., lateral cracks simulated by steps of various depths). As can be clearly seen, the thinner steps (oriented toward the top of the image) scatter a significantly larger portion of the incident light back toward the detection system. The relationship between scatter intensity and subsurface "crack" depth is quantified in the plot of Fig. 5, which shows a good match to the theoretically predicted exponential decay of sensitivity to defects with increasing depth. Note that for these step-wedges the exponential behavior only applies above a certain depth, because below that depth there is insufficient material to generate completely diffuse scatter, resulting in incomplete randomization of the light polarization. In the limit, as the depth approaches zero, the subsurface back-scattered intensity will therefore also approach zero. While this behavior is not evident in Fig. 5 for the more "attenuative" materials, it is seen for the least-scattering material, GS44. Note, however, that because this effect results from the infinite "thickness" of the simulated crack, this zero-depth limit will be equal to the infinite-depth limit in a real subsurface crack (given as 100 in Fig. 5). Also seen in Figs. 4a and 4c are local regions of lower or higher intensity (located in the second thinnest

Figure 2. Diagram of experimental arrangement for 2-D subsurface/surface laser scatter inspection of ceramic components.

Figure 3. Diagram of laser scatter 2-D image acquisition method.

Figure 4. 2-D laser scatter scans of step-wedges made from (a) GS44, (b) SiAlON, and (c) NT164.

step of 4a and the thickest step of 4c, respectively). While no destructive analysis could be performed on these specimens, experience has shown that signatures of this sort are generally indicative of subsurface inclusions and voids, respectively.

The images in Fig. 4 suggest a substantial interaction between subsurface cracks and scattered laser light. However, the step-wedge configuration can simulate only lateral cracks (i.e., those parallel with the surface). To expressly identify the manifestation of this interaction with median cracks (i.e., those perpendicular to the surface), a modification to the experimental configuration must be made. However, by comparing the scatter images of Fig. 4, one can obtain an idea as to the form of such interaction. Figure 4a shows the distribution of laser scatter for the least scattering material (and hence the material with the greatest penetration depth), GS44. This image shows a substantial edge-affected region in which the scattered intensity drops off as an edge is approached. This is caused by the loss of scattered light through the side of the specimen. Thus, by measuring the width of this "edge-affected zone," one can determine the lateral extent of the subsurface-generated back-scatter. As expected, the width of this zone is greatest in the GS44 step-wedge (which has the greatest penetration depth) and narrowest in the SiAlON specimen (which has the lowest penetration depth).

Based on the edge-affected zone behavior, it appears that the best way to detect the depth of subsurface median cracks is to measure both the intensity and the lateral extent of subsurface scatter. A design modification to the current system is therefore under development. In the meantime, additional improvements will be made in the automation software to decrease acquisition time and to allow inspection of nonpredetermined (i.e., user-defined) geometries.

Figure 5. Plot of average back-scattered intensity from each step of the step-wedges shown in Fig. 2. Drawn lines are exponential curves best-fit to the data.

Part 2: Dye Penetrant

A. Literature review and state-of-the-art assessment.

Detection of surface cracking via dye penetrants is a well-developed technology and ASTM/ASME standards are available on the subject. ASTM E165-91 (Standard Test Method for Liquid Penetrant Examination) covers the basic methods for penetrant examination of nonporous materials such as metals, glass and other ceramics, and some plastics. This standard is supplemented by a group of standards that cover different penetrant and developer types. ASTM E165-91 does not specifically address safety problems related to the use of any materials and leaves this responsibility to the user. ANL's inspection department uses dye penetrant material in small amounts from spray cans. They follow the safe-handling procedures listed on the Material Safety Data Sheet from the manufacturer. This mainly involves ventilation and protective masks if needed.

Many manufacturers of metal parts routinely use dye penetrants for crack detection in one or more steps of their manufacturing process, and they are continually attempting to upgrade the process for (a) greater sensitivity and (b) lower costs, especially those associated with safe disposal of test materials.^{1,2} Because of these environmental disposal concerns, several vendors are reformulating their dye penetrant systems to eliminate fluorocarbons. We have found that dye penetrants are not as widely used in ceramic manufacturing even though special products are available. Discussions with several ceramic manufacturers revealed that they use mostly "standard" dye penetrant techniques for surface crack detection. Fluorescent postemulsified methods with ultra-high-sensitivity penetrants are preferred. Two additional examples are Sherwin-DP-52 and Magnaflux P1A Partex, which have been developed specifically for the

ceramics market. However, all ceramic component manufacturers expressed a need for better dye penetrant technology. An unresolved question currently being addressed is whether some dye penetrant materials, especially liquids, leave a residue that will interfere with subsequent tests.

B. Comparison of penetrant methodologies.

To capture images of dye penetrant inspection with a 512 x 512 eight bit digital camera, a 486-33 computer with a Data Translation frame grabber board has been set up. Digital enhancement of images is occasionally used to improve crack detection.

A new gas capillary diffusion method of crack detection is under development at the Institute of Chemical Physics in Moscow, Russia.³ This technique, demonstrated at ANL in January by Dr. Nadjia Beriozkina, one of the inventors, may improve detection of finer cracks than possible with large-molecule liquid penetrants. The method uses ammonia gas to diffuse into cracks. A treated paper is then laid over the cracked surface, where it changes color in response to the ammonia in a manner very similar to that seen in litmus paper. For small test pieces, samples are placed in a plastic bag that is then filled with ammonia gas (Fig. 6). After 5-10 min., the samples are removed. The special detector paper is pressed against the surface to be tested for about 1 min. The resulting reaction of the ammonia from the cracks with the paper provides a mirror image of any crack pattern on that surface. Because the ammonia is reasonably volatile, the image does not remain on the paper very long, and we therefore set up a video digitizing system to capture the images. We examined several specimens, as noted below in Table 1. (One added benefit of capturing the images in this way was that the mirror-reversal inherent in the method could also be removed.)

Figure 6. Schematic diagram showing infiltration (with slight overpressure) during gas capillary diffusion dye penetrant testing.

A second protocol for using the gas diffusion method with larger samples uses liquid saturated with the ammonia gas. The liquid is brushed on the surface, allowed to stand for a few minutes, and then wiped off. Immediately, the sensing paper is applied. This method was applied to the front surface of one of the ZrO_2 specimens and the sensing paper applied to the back surface to detect through-cracks. The resulting crack pattern did not match the front pattern well. This was attributed to a network of cracks between the front and back surfaces.

Table 1. Ceramic Specimens Used in Initial Gas Capillary Diffusion Dye Penetrant Study

Material	Specimen ID	Dimensions	Condition
SiAlON	1-2	6.35 cm OD tube	Thermally shocked 1200°C-water (2 cycles)
SiAlON	3-4	6.35 cm OD tube	Thermally shocked 1200°C-water (1 cycle)
SiAlON	5-6	6.35 cm OD tube	as received
ZrO ₂		Standard Flexure Bars (3 x 4 x 50 mm)	Thermally shocked 300°C-water (1 cycle)
ZrO ₂		Standard Flexure Bars	Thermally shocked 350°C-water (1 cycle)
ZrO ₂		Standard Flexure Bars	Thermally shocked 550°C-water (1 cycle)
ZrO ₂		Standard Flexure Bars	Thermally shocked 1000°C-water (1 cycles)
ZrO ₂		Standard Flexure Bars	as received

As noted earlier, the resulting patterns on the sensing paper fade with time, sometimes within minutes. Additional development is needed to produce a more stable sensing medium. The materials necessary for this technique are not currently available commercially. A small U.S. company, Marotta Scientific of Montville, N.J., has obtained rights for distribution in the U.S. and is planning to develop a commercial product.

Another technique investigated was the charged-particle method. Statiflux material and equipment for crack detection in dielectric materials was obtained.⁴ In this technique a charged powder is sprayed onto a dielectric surface and collects along discontinuities in the dielectric field. The usual protocol is to simply spray the specimen of interest with the charged powder. For better resolution, the protocol is modified by brushing an electrolyte liquid (salt solution) over the surface before the powder spray. This provides a conducting path so opposing charges may collect in the cracks to more firmly attract the charged powder.

Figure 7 is a comparison of three methods of surface crack detection, all applied to the same sample piece, a thermally stressed (thermally shocked) tubular section of SiAlON. Figure 7a shows the results of using a visible dye penetrant with developer. The developer pulls the penetrant out of cracks by capillary action; deeper cracks will result in wider indications. Figure 7b shows the results of the gaseous diffusion technique. The image is actually that of the sensitive paper immediately after removal from the ceramic's surface. Figure 7c shows the Statiflux-treated surface. In this sample surface cracks were visible under a microscope at 20x, but the Statiflux image is the only one of the three to reveal all of the visibly detected cracks. The other two methods detected only the deeper cracks.

In an attempt to produce a standard to allow detection sensitivity comparison, a flat surface of silicon carbide is being polished (to $\leq 0.8 \mu\text{m}$) and then indented with a Vickers microhardness tester. Various loads are applied to establish which will yield a satisfactory standard. We will also explore different surface finishes to establish the impact of that variable as well. The resulting microcracks on these standards will be used to compare the sensitivity of the various dye penetrant methods and protocols.

(a)

(b)

(c)

Figure 7. Comparison of dye penetrant methods: (a) Visible dye penetrant, (b) gaseous diffusion, and (c) Statiflux.

Status of Milestones

Determine optical properties of SiAlON and GS-44 for optimum optical detection parameters (polarization, wavelength, angle of incidence, etc.).

Completed February 28, 1994

All others are on schedule.

Communications/Visits/Travel

Attended

W.A. Ellingson attended and participated in the Project Review and Coordination Meeting of the Cost-Effective Ceramic Machining Project, September 8, 1993 at Oak Ridge, TN.

W. A. Ellingson (on behalf of J. S. Steckenrider) presented a paper titled, "Application of Laser Scattering for Detection of Surface and Subsurface Defects in Si₃N₄ Components," at the Am. Cer. Society 18th Annual Cocoa Beach, Mtg., Cocoa Beach, FL, Jan. 12-17, 1994

Planned

W.A. Ellingson plans to present an invited paper titled "Nondestructive Characterization of Structural Ceramic Components" to the 5th International Symposium on Ceramic Materials and Components for Engines, Shanghai, China, May 29-June 1, 1994.

Problems Encountered

None.

Publications

None.

References

1. R.J. Malins, D. McCall, and G. W. Rhodes, "Systems Level Considerations for Environmentally Responsive Fluorescent Penetrant Testing," *Mat. Eval.*, March 1993, pp. 338-351.
2. S.J. Robinson, "Here Today, Gone Tomorrow: Replacing Methyl Chloroform in the Penetrant Process," *Mat. Eval.*, August 1992, pp. 936-946.
3. Beriozkina, N.G., Larichev, M.N., Leipuvsky, I.O., Eremin, G.L. and Dergunov, N.N., Indicator Capillary - Diffusion Method for Non-Destructive Defectoscopy of Composite Materials, Institute of Energy Problems of Chemical Physics, USSR Academy of Sciences.
4. Manufactured by Stresscoat, 14 N. Brenson Ave., Upland, CA 91786.

2.0 MATERIALS DESIGN METHODOLOGY

INTRODUCTION

This portion of the project is identified as project element 2 within the work breakdown structure (WBS). It contains three subelements: (1) Modeling, (2) Contact Interfaces, and (3) New Concepts. The subelements include macromodeling and micromodeling of ceramic microstructures, properties of static and dynamic interfaces between ceramics and between ceramics and alloys, and advanced statistical and design approaches for describing mechanical behavior and for employing ceramics in structural design.

The major objectives of research in Materials Design Methodology elements include determining analytical techniques for predicting structural ceramic mechanical behavior from mechanical properties and microstructure, tribological behavior at high temperatures, and improved methods for describing the fracture statistics of structural ceramics. Success in meeting these objectives will provide U.S. companies with methods for optimizing mechanical properties through microstructural control, for predicting and controlling interfacial bonding and minimizing interfacial friction, and for developing a properly descriptive statistical data base for their structural ceramics.

2.2 CONTACT INTERFACES

2.2.2 Dynamic Interfaces

Development of Standard Test Methods for Evaluating the Wear Performance of Ceramics

P. J. Blau (Oak Ridge National Laboratory)

Objective/scope

The goal of this effort is to improve consistency in reporting ceramic wear data by helping to develop one or more standard test methods for quantitatively determining the wear resistance of structural ceramics, in reciprocating sliding, a type of motion which is experienced by several types of automotive and truck engine wear parts. ORNL is working with the American Society for Testing and Materials (ASTM) in meeting this objective. Wear-test development normally falls within the scope of ASTM's G-2 Committee on "Wear and Erosion," and in 1990, P. J. Blau was appointed chairman of a newly established Task Group G02.40.07, "Reciprocating Sliding Wear Testing," within the G-2 Committee. This report describes the continuing activities of the Task Group.

Technical highlights

An ASTM G-2 meeting was held on December 10-11, 1993, at the Dallas/Fort Worth, Texas, airport. Revisions to the draft standard were discussed, as were the results of the second interlaboratory testing program. The draft standard will be reballoted prior to the next meeting in Montreal in May 1994.

Silicon nitride wear test specimens of the same composition as were used in the first interlaboratory program were circulated to eight laboratories for the second interlaboratory ("round-robin") testing program. The participants were: ORNL, General Motors R&D Center (two different departments), Cummins Engine Company, Caterpillar Tech Center, National Research Council - Canada, Cameron-Plint Ltd. - United Kingdom (a wear machine manufacturer), and National Physical Laboratory - United Kingdom. Each test kit contained two polished, flat specimens of sintered reaction-bonded silicon nitride (provided by Eaton Corporation), one numbered test ball of bearing-grade NBD 200 silicon nitride, and a small bottle of mineral oil. Test conditions were: normal force, 200 N; sliding frequency, 10 Hz; stroke length, 10 mm; test duration, 33:40 (200-m sliding distance); and lubrication by immersion in a mineral oil bath at 150°C.

Data from only five of the eight laboratories were acceptable for the statistical evaluation. Two laboratories failed to conduct the tests at all, and one laboratory did not follow the testing instructions correctly. Table 1 lists the results of the valid tests. Friction coefficients were extremely repeatable and reproducible. The ball wear and flat specimen wear volumes were less so; however, the repeatability (within laboratory) was not unreasonable for wear test results. The data in Table 1 will be included in an Appendix to the draft standard.

References

None.

Table 1. Results of Lubricated Wear Tests of Silicon Nitride Specimens (five laboratories)

Statistical Quantity	COF	Ball Diam (mm)	Ball Vol* (mm ³)	Flat Vol (mm ³)
			× 10 ³	× 10 ³
Average	0.1546	0.7488	3.386	3.624
Std. dev. between cells	0.00759	0.0398	0.798	2.267
Repeatability std. dev.	0.00403	0.0554	1.348	0.938
Reproducibility std. dev.	0.00835	0.0623	1.414	2.408
Variation in SD between cells (%)	4.91	5.32	23.57	62.56
Variation in repeatability SD (%)	2.61	7.40	39.81	25.88
Variation in reproducibility SD (%)	5.40	8.32	41.76	66.45

*Note: The ball wear volume is derived from the scar diameter.

Status of milestones

- 222206 Make revisions to the first ballot and submit to ASTM G-2. Completed June 30, 1993.
- 222207 Complete reduction of data from the second set of round-robin wear tests. Completed December 1993.
- 222208 Revise and resubmit draft for subcommittee balloting. Completed January 1994.
- 222209 Address any negatives and comments on the subcommittee ballot and prepare for discussion at the G-2.40 meeting, May 1994 (continuing).

Communications/visits/travel

P. J. Blau attended the ASTM G-2 Committee meeting in Dallas/Fort Worth, Texas, on December 10-11, 1993, to lead the Task Group meeting on "Reciprocating Sliding Wear Testing."

Publications/presentations

None.

2.3 NEW CONCEPTS

Advanced Statistical Concepts of Fracture in Brittle Materials

C. A. Johnson and W. T. Tucker (General Electric Corporate Research and Development)

Objective/Scope

The design and application of reliable load-bearing structural components from ceramic materials requires a detailed understanding of the statistical nature of fracture in brittle materials. The overall objective of this program is to advance the current understanding of fracture statistics, especially in the following four areas:

- Optimum testing plans and data analysis techniques.
- Consequences of time-dependent crack growth on the evolution of initial flaw distributions.
- Confidence and tolerance bounds on predictions that use the Weibull distribution function.
- Strength distributions in multiaxial stress fields.

The studies are being carried out largely by analytical and computer simulation techniques. Actual fracture data are then used as appropriate to confirm and demonstrate the resulting data analysis techniques.

Technical Highlights

During this reporting period a study of the Phase III data on the Norton contract for the Ceramic Technology Project published in the final report ORNL/Sub/89-SB182/1 (Ref. 1) was completed. The purpose was to investigate the individual failure modes (Machining, M, Inclusion, I, Amorphous, Am, Microporosity, Mp, and Unknown, U) identified by fractography in the study of 320 specimens carried out by Norton. Censored data methods have been employed to study the four competing failure modes: M, I, Am, and Mp. Preliminary studies indicated that a 2-parameter Weibull adequately fits the M, I, and Mp failure modes. However, there is a distinct lack of fit to a 2-parameter Weibull for the Am failure mode.

The preliminary results have been discussed with Norton personnel and are studied in more depth herein. Figure 1 gives a plot of the Intrinsic failure mode designation described in Ref. 1, where the solid line is given from Norton's three parameter, censored Weibull fit to the Intrinsic failures. The plot agrees with Figure 17 of Ref. 1. Maximum likelihood (ML) analysis of the same data yields slightly different, but comparable, estimates than those obtained via least squares by Norton. Norton's reported values are $\hat{m} = 3.92$, $\hat{\sigma}_\theta = 444$, and $\hat{\mu} = 665$. The corresponding MLE's are $\hat{m} = 3.57564$, $\hat{\sigma}_\theta = 417.881$, and $\hat{\mu} = 6990.094$. While exact statistical tests have yet to be developed, it is clear that the Intrinsic failure mode is not given by a 2-parameter Weibull distribution.

In order to further study the nature of the Intrinsic mode, censored analyses of the Amorphous and Microporosity data were carried out. In these studies the Unknown failure mode observations were deleted. This is acceptable if the unknown modes act in a manner that is independent of the other failure modes--one is in effect assuming that the unknown failure

mode strengths were selected at random from the set of 320 observations. The results are shown in Figures 2 and 3, which give, respectively, the analyses of the Amorphous and Microporosity failure strengths. Study of these figures indicates that the lack of fit of the Intrinsic mode to a 2-parameter Weibull is due to the Amorphous mode. Again exact statistical tests are not available, but it is clear that the Microporosity strengths fit a straight line very well in the Weibull plot. Moreover, this is not the case for the Amorphous mode. However, the fact that a 2-parameter Weibull is inadequate for this mode is not grounds to conclude that a 3-parameter Weibull is the desired alternative. This is a complex issue that needs further study with Norton. Indeed a ML censored analysis (not shown) of the data employing a lognormal distribution gives just as good a statistical fit to the data as does a 3-parameter Weibull. The "weaker" strengths of the Amorphous failure mode are diminished from what should be observed if the underlying distribution were a 2-parameter Weibull, but it may well be that there is no lower bound failure strength.

References

1. V.K. Pujari, D.M. Tracey, M.R. Foley, N.I. Paille, P.J. Pelletier, L.C. Sales, C.A. Wilkens, and R.L. Yeckley, "Development of Improved Processing and Evaluation Methods for High Reliability Structural Ceramics for Advanced Heat Engine Applications, Phase I," *ORNL/sub/89-SB182/1*, Ceramic Technology for Advanced Heat Engines Project Final Report, U.S. Department of Energy Contract DE-AC05-84OR21400, Subcontract 86X-SB182C, August 1993.

Status of Milestones

All milestones are on schedule.

Communications/Visits/Travel

None.

Problems Encountered

None.

Publications

None.

Weibull Probability Plot:

Norton NCX-5102 Tensile Data

Figure 1 — Plot of Intrinsic Failure Mode Showing Norton 3P Fit

Weibull Probability Plot:

Norton NCX-5102 Tensile Data

Figure 2 — Plot of Amorphous Failure Mode Showing ML 2P Fit

Weibull Probability Plot:

Norton NCX-5102 Tensile Data

Figure 3 — Plot of Microporosity Failure Mode Showing ML 2P Fit

3.0 DATA BASE AND LIFE PREDICTION

INTRODUCTION

This portion of the project is identified as project element 3 within the work breakdown structure (WBS). It contains five subelements, including (1) Structural Qualification, (2) Time-Dependent Behavior, (3) Environmental Effects, (4) Fracture Mechanics, and (5) Nondestructive Evaluation (NDE) Development. Work in the Structural Qualification subelement includes proof testing, correlations with NDE results and microstructure, and application to components. Work in the Time-Dependent Behavior subelement includes studies of fatigue and creep in structural ceramics at high temperatures. Research in the Environmental Effects subelement includes study of the long-term effects of oxidation, corrosion, and erosion on the mechanical properties and microstructures of structural ceramics. Work in the Fracture Mechanics subelement includes development of techniques for measuring the tensile strength and creep resistance of ceramic materials at high temperatures, and testing ceramic materials at high temperatures under uniaxial tension. Work in the NDE Development subelement is directed at identifying approaches for quantitative determination of conditions in ceramics that affect their structural performance.

Major objectives of research in the Data Base and Life Prediction project element are understanding and application of predictive models for structural ceramic mechanical reliability, measurement techniques for long-term mechanical property behavior in structural ceramics, and physical understanding of time-dependent mechanical failure. Success in meeting these objectives will provide U.S. companies with the tools needed for accurately predicting the mechanical reliability of ceramic heat engine components, including the effects of applied stress, time, temperature, and atmosphere on the critical ceramic properties.

3.1 STRUCTURAL QUALIFICATION

Microstructural Analysis of Structural Ceramics

B. J. Hockey and S. M. Wiederhorn

(National Institute of Standards and Technology)

Objective/Scope

The objective of this part of the program is to identify mechanisms of failure in structural ceramics subjected to mechanical loads at elevated test temperatures. Of particular interest is the damage that accumulates in structural ceramics as a consequence of high temperature exposure to stresses normally present in heat engines.

Design criteria for the use of ceramics at low temperature differ from those at high temperature. At low temperature ceramics are elastic and brittle; failure is controlled by a distribution of flaws arising from processing or machining operations, and the largest flaw determines the strength or lifetime of a component. By contrast, at high temperature where ceramics are viscoelastic, failure occurs as a consequence of accumulated, or distributed damage in the form of small cavities or cracks that are generated by the creep process. This damage effectively reduces the cross-section of the component and increases the stress that must be supported. Such increases in stress are autocatalytic, since they increase the rate of damage and eventually lead to failure as a consequence of loss in cross section. When this happens, the individual flaw loses its importance as a determinant of component lifetime. Lifetime now depends on the total amount of damage that has occurred as a consequence of the creep process. The total damage is now the important factor controlling lifetime.

Recent studies of high temperature failure of the non-oxide ceramics intended for use for heat engines indicates that for long term usage, damage accumulation will be the primary cause of specimen failure. Mechanical defects, if present in these materials, are healed or removed by high temperature exposure so that they have little influence on long term lifetime at elevated temperature. In this situation, lifetime can be determined by characterizing the damage and the rate of damage accumulation in the material at elevated temperatures. In ceramic materials such as silicon nitride and SiAlON, such characterization required high resolution analyses because of the fine grain size of these materials: hence the need for transmission electron microscopy as an adjunct to the mechanical testing of ceramics for high temperature applications is apparent.

In this project, the creep and creep-rupture behavior of several ceramic materials will be correlated with microstructural damage that occurs as a function of creep strain and rupture time. Materials to be studied include: SiAlON; hot-pressed silicon nitride; sintered silicon carbide. This project will be coordinated with WBS 3.4.1.3, Tensile Creep Testing, with the ultimate goal of developing a test methodology for assuring the reliability of structural ceramics for high temperature applications.

Technical Highlights

Analytical Transmission Microscopy has been used to study cavity damage produced during tensile creep in different grades of silicon nitride. Part of this effort was directed at explaining the significant decrease in interfacial cavitation in Norton NT-154 when the creep temperature is increased to 1400 C. and above. In brief, tensile creep at 1400C. and above is found to result in interfaces containing relatively thick (up to 10 nm) glassy layers. Although the interfaces do not appear to have been uniformly displaced, the results do indicate that fully accommodated (by the diffusive influx of glassy phase) interfacial displacements become possible with increased temperature. Additional results were also obtained on the formation of cavities within multi-grain junctions. The results confirm that these cavities, which can range in size from 0.1 to 1.0 microns, result from cavity growth within the second phase contained in regions interstitial to the silicon nitride grains. Recent results have also confirmed that such interstitial cavitation occurs in all grades of silicon nitride studied in this program (NT-154, GN-10, AY-6 and PY-6) and, thus appears inherent to the creep deformation of two-phase materials.

Experimental Technique

The results of this study were obtained by analytical transmission microscopy (ATEM). ATEM was used to examine samples of GTE AY-6 and PY-6, Garrett GN-10, and Norton NT-154 silicon nitride which had been subjected to tensile creep under the tensile test task of this project (WBS 3.4.1.3). Standard ceramographic techniques were used to prepare specimens for ATEM analysis.

Results and Discussion

During the past six months, studies on the effect of microstructure on the creep/creep rupture of silicon nitride were continued. Additional results on cavitation during tensile creep were obtained for each of the four different grades of silicon nitride used in this study.

For Norton NT-154, particular emphasis was placed on examining narrow, two grain interfaces in samples crept at 1400 and 1430 C. As previously reported, creep at 1400 C and higher results in limited interfacial cavitation in this material, whereas creep at lower temperatures results in high densities of discrete, lenticular cavities on narrow (1nm or less in width) interfaces oriented nearly normal to the tensile stress axis. It was also reported that the formation of interfacial cavities is preceded by the development of localized pockets of accumulated glass (of roughly yttrium disilicate composition) containing detectable concentrations of chlorine. Recent results indicate that the reduction in interfacial cavities produced at 1400 C. and above relates to a change in this precursor stage. At temperatures below 1400 C., multiple, small pockets of glass are formed within individual interfaces; each pocket generally measuring 2 to 3 nm. normal to the interface and 100 nm. along the interface. Cavity nucleation occurs within these small pockets of glass and subsequent growth into

the silicon nitride grains results in lenticular shaped cavities, usually with maximum dimensions of 250 nm. At creep temperatures of 1400 C. and above, the formation of multiple, small pockets of accumulated glass is rare. Instead, interfaces tend to exhibit evidence of accumulated glass (or, alternatively, interface widening) over a single, large area. As illustrated in Fig. 1, these pockets of accumulated glass generally extend 200 to 500 nm. along the interface and from 2-3 to 10 nm. normal to the interface. Here, the term "pocket" is retained because there is no apparent increase in interfacial width over the remaining portion of the interface. As such, their formation does not appear to be the direct result of rigid grain displacement accompanied by flow or transport of glass into the interface. Finally, while the glass within these large pockets also contains measureable concentrations of chlorine, no evidence has been found for cavity nucleation within the glass or for fully developed, crack-like cavities, reflecting the morphology of these large glassy pockets.

For the other grades of silicon nitride, namely GTE AY-6 and PY-6 and Garrett GN-10, attention was directed at determining the occurrence and relative extent of interstitial cavitation. Here, the term "interstitial cavitation" refers to cavity formation within the pockets of residual second phase, which are located at the interstices of the silicon nitride grains, i.e., triple and multi-grain junctions. Past results on NT-154 by both TEM and SAXS have shown that these cavities form the bulk of cavity damage produced during creep and that the volume fraction of cavities increases lineary with strain. Our more recent TEM observations on AY-6, GN-10, and PY-6 indicate similar results apply to these materials as well. Moreover, because these grades contain a larger volume fraction of second phase than NT-154, interstitial cavitation should play a major role in the creep rupture process. The effect of increased second phase content on interstitial cavitation is reflected in Figure 2, a and b. Here, it should be noted that the bulk of retained second phase in these materials is found in regions of the microstrure containing small (0.5 micron), silicon nitride grains, and the increased content of second phase is primarily reflected in the size of fine-grained, second phase-rich regions. In NT-154 and, to an extent, PY-6, these regions are smaller and more uniformly distributed; interstitial cavities, thus, are more uniformly distributed, even for large cavity sizes and large strains, Fig. 2 a. In AY-6 and GN-10, these fine-grained, second phase-rich regions have dimensions rivalling the largest grains in these materials, and cavitation of the second phase results in large, highly porous regions, Fig. 2 b.

The common occurrence of interstitial cavitation in these different grades of silicon nitride relates to the fact that each can be similarly described in terms of densely-packed "rigid" grains (silicon nitride) and a "softer" matrix (the second phase, whether glassy or crystalline). As is well known, such close-packed, two phase systems exhibit dilatency during deformation; effectively, the rigid-body displacements of the close-packed grains results in an increase in volume or, alternatively, dilation of the intergranular phase. Accordingly, tensile creep results in the development of hydrostatic tension within the second phase and ultimately results in cavitation

Figure 1a. Wide two-grain interface in NT-154 after creep at 1430 C.; tensile stress axis normal to interface. Thick glassy interphase (dark contrast) extends over large portion of interface.

Figure 1b. Higher magnification view of same interface; glassy interphase thickness estimated to be 6 to 11 nm.

Figure 2a. Interstitial cavities in NT-154 after creep at 1400 C. Despite micron size dimensions, cavities are widely distributed.

Figure 2b. Interstitial cavities in AY-6 after creep at 1250 C. Cavity growth within the second phase results highly porous domains of large dimensions.

within the pockets of second phase (multi-grain junctions) as well as within two-grain interfaces.

Status of Milestones

On schedule

Publications

"Creep Damage Mechanisms in Silicon Nitride", S. Wiederhorn, W. Lucke, B. Hockey, and G. Long. Proceedings of a Workshop on Tailoring of High Temperature Properties of Silicon Nitride Ceramics. Held Oct. 6-9, 1993. Schloss Ringberg, F.R.G.

Mechanical Properties and Microstructural Characterization of Si₃N₄ Ceramics

T. A. Nolan and K. L. More

Objective/scope

The objective of the research is to use analytical and high-resolution electron microscopy to characterize the microstructures of several silicon nitride materials and cutting tool materials. This report will focus on the analysis of a recently received diamond/silicon carbide cutting tool material manufactured by Diasil ADC and the analysis of a self-reinforced silicon nitride/SiAlON ceramic, NT-451, manufactured by Saint-Gobain Norton.

Technical highlights

DIASIL Cutting Tool Material

A limited amount of Diasil-ADC (manufactured by Crestel Pty. Ltd.) was received for microstructural characterization in late October 1993. Diasil-ADC is a diamond/SiC composite used primarily as a cutting tool material. In order to prepare samples of Diasil-ADC for examination in the scanning electron microscope (SEM) and transmission electron microscope (TEM), the disc was cut into thin slices by electrical discharge machining (EDM). The thin slices were then polished using 6- μm diamond paste followed by 1- μm diamond paste.

A polished surface was examined in the SEM, a typical low-magnification image of which is shown in Fig. 1. The large particles (arrowed) are the single-crystal diamond particles. By performing image analysis on several similar SEM images, these large particles were found to average approximately 90 μm in size (fitted ellipse long axis) and to occupy approximately 63 vol %. There was also a distribution of much smaller diamond particles between these large particles which averaged about 5 μm in size (fitted ellipse major axis) and occupied an additional 10 vol %. These particles are shown in the SEM image (arrowed) in Figs. 2 and 3. Thus, the diamond constituted 73% of the Diasil-ADC, which agrees well with that reported in the Crestel Pty. Ltd. literature for Diasil-ADC (composite material reported to contain approximately 75% diamond). The morphology of the diamond particles changed with size; the large particles were primarily elongated and faceted, whereas the small particles were more rounded (compare Figs. 1 and 3).

A TEM specimen was also prepared by cutting a 2- by 2-mm square from the polished slice which was ground to 200 μm in thickness using 30- μm diamond paste, polished using 6- μm diamond, mounted on a 3-mm carbon ring, and ion milled for many hours (>50 h). Since the specimen was so hard, it could not be dimpled using conventional techniques. The TEM analysis will be conducted to determine the exact nature of the matrix, which is assumed to be polycrystalline SiC. X-ray diffraction (XRD) results indicate that the composition of the Diasil-ADC is not as simple as expected, as the material contains an additional minor matrix phase(s). Initial TEM examination was consistent with the SEM results; however, the specimen needed additional thinning in the ion mill. The specimen is currently undergoing thinning and TEM viewing iterations to optimize the amount of thin area in the specimen.

Fig. 1. Low-magnification SEM image of a polished surface of Diasil-ADC (several large single-crystal diamond particles are arrowed).

Characterization of NT-451 SiAlON

During the last reporting period, several samples of NT-451 were acquired and analyzed. Samples included portions of a billet and several reciprocating engine valves. NT-451 is a principal candidate for manufacture of valves and other components for replacement in reciprocating engines in an effort to reduce mass and improve efficiency. Laboratory mechanical testing under various conditions has begun. A complete microstructural characterization of the material was undertaken in order to determine the changes associated with testing and engine use.

Scanning electron microscopy (SEM) of a fracture surface of NT-451 (see Fig. 4) shows a "typical" microstructure of a self-reinforced Si_3N_4 ; large, acicular grains are surrounded by smaller, nearly equiaxed grains. A transmission electron micrograph (TEM) of a typical field of an ion-milled thin foil of this material is shown in Fig. 5. TEM reveals that there are two principal constituents, single-crystal grains of Si_3N_4 with amorphous material at "triple-point" pockets and present as a thin film between grains. No evidence for any devitrification was found. Energy dispersive x-ray analysis (EDS) revealed both aluminum and yttrium in the grain boundary glass (see Fig. 5). Thus, yttrium and aluminum compounds are used as sintering aids in the manufacture of this material. XRD supported the above; only one crystalline phase with peaks close to those of $\beta\text{-Si}_3\text{N}_4$ was identified. Quantitative SEM of metallographically polished and plasma-etched specimens indicated about 15 vol % glass in NT-451.

Fig. 2. SEM image of smaller diamond particles (arrowed) between large diamond particles.

Considerable effort was expended to determine to what degree NT-451 was a SiAlON. The XRD data indicated that the major phase was "nearly" β - Si_3N_4 but with a very small peak shift toward the positions of a silicon-rich SiAlON structure $\text{Si}_{1.4}\text{Al}_3\text{O}_3\text{N}_{20}$ (JCPDS #41-1013). Numerous grains were analyzed by EDS in the TEM, and the resulting spectra were matched to calculated spectra. The best composition fit was $\text{Si}_{2.85}\text{Al}_{0.15}\text{O}_{0.3}\text{N}_{3.7}$ or an aluminum-to-silicon ratio of approximately 1 to 20.

No difference in structure or composition was found between the billet or the valves. Based upon the above results, NT-451 appears to be a good candidate for intermediate temperature use (below 1000°C) in reciprocating engines. With mechanical testing under way, it should soon be possible to determine the effects of temperature and stress on structure and composition.

Status of milestones

Program on schedule.

Communications/visits/travel

1. T. A. Nolan, K. L. More, L. F. Allard, M. K. Ferber, and D. W. Coffey, "Microstructural Characterization of Silicon Nitride Intended for Use in Reciprocating Engines," presented at the 96th Meeting of the American Ceramic Society, Indianapolis, Indiana, April 24-28, 1994.

Problems encountered

None.

Fig. 3. SEM image of small diamond particles which averaged approximately 5 μm in size.

Fig. 4. A typical fracture surface of NT-451 shows a micro-structure consisting of large, acicular grains surrounded by smaller, more equiaxed grains.

Fig. 5. Typical microstructure of NT-451 as observed by TEM showing crystalline grains surrounded by amorphous grain boundary material containing Al, Si, Y, O, and probably some N, as determined by EDS (top left). The crystalline phase is a SiAlON with an Al-to-Si atomic ratio of about 1 to 20 (top right). (Carbon results from contamination during the EDS analysis.)

Project Data Base

B. L. Keyes (Oak Ridge National Laboratory)

Objective/scope

The objective of this task is to develop a comprehensive computer database containing the experimental data on properties of ceramic materials generated in the total effort. This computer system should provide a convenient and efficient mechanism for the compilation and distribution of the large amounts of data involved. The database will be available in electronic form to all project participants. In addition, periodic hard-copy summaries of the data, including graphical representation and tabulation of raw data, will be issued to provide convenient information sources for project participants.

Technical highlights

Work began on revising two pieces of software from AlliedSignal to work on IBM PC-compatible microcomputers. CERAMIC computes estimates for Weibull parameters with confidence bounds, and for a particular specimen or component, calculates values of, and confidence bounds on, reliability at a given stress and allowable stress for a desired reliability. ERICA computes multiaxial and stress gradient factors by numerical integration based on the results of an Ansys stress analysis of the component and the probability of failure due to fast fracture or slow crack growth based on I, Weibull parameters, and other material properties. The original versions of both programs were written and compiled on a Cyber 2000 using CalComp plotting routines and IMSL math routines. Most PC users have neither Calcomp plotters nor access to the proprietary IMSL libraries, so routines relating to these items were being replaced with more PC-oriented routines, including some tested equivalent public-domain math routines obtained from NETLIB. Some of the site-specific code has been replaced with the more universal ANSI-77 code. Many of the single-precision variables were changed to double precision because of the differences in word length on the two computers (Cyber uses 64-bit words; PCs and VAXes use 32-bit words). All data routed to the plotters have been, for now, routed to a text file.

Both programs were to be run on the ORNL STC VAX for debugging prior to porting to the PC because the VAX FORTRAN compiler could handle the voluminous program and memory requirements better. The VAX results, when verified as being correct, would be used to check the PC version. However, work on the programs was suspended when the decision was made to wait for AlliedSignal to release the workstation version later in the year.

Also, during this period, numerous micrographs were scanned into the system for inclusion in the database. The cataloging/indexing process is time consuming because it is performed on two computers of differing platforms using different software packages (a necessary step we hope to change soon). A text index is included in the Ceramic Technology Program (CTP) database to acquaint the user with available pictures. The actual graphics files are located on an Apple Macintosh because of the graphics capabilities of the Mac. PICT/PIC, TIF, and EPS files have been transported across platforms successfully and incorporated into reports with no loss of resolution.

A database requestor with a new computer and very little software inspired creation of a stripped-down version of the computerized user interface. This new program is a stand-alone product that runs on PC-compatible systems and is shipped with the dBASE IV™

RUNTIME modules needed. Although not as extensive in features and capabilities as the full interface will be, this version allows the user to search files for specific materials by name and/or class (silicon nitrides, silicon carbides, aluminas, etc.); to subset the data into text, Lotus 1-2-3, or dBASE IV files; or to send output directly to the printer. This program has no analysis capabilities and searches only one file at a time but will perform interim searches and saves. The full version will have many more capabilities when completed.

Conversion of the database and associated programs on the PC-compatible from dBASE IV to Foxpro™ began during March 1994. Similarities between dBASE and Foxpro have facilitated the transition, but differences in some of the screen-formatting routines have slowed the process. Foxpro is a much more powerful program with a more versatile programming language for the developer. The primary reason for conversion is that the new database and software should be completely compatible across the PC-compatible—Macintosh platform lines, a major consideration in this multi-platform society. Foxpro also has some capabilities for handling graphics within the database, thus permitting incorporation of the existing photomicrograph database that currently resides on the Macintosh only. Conversion will continue as time permits.

Database personnel are involved in developing an American Society for Testing and Materials (ASTM) guideline document (for the E-49 Committee on Computerized Materials Databases) on ceramic material designations for computer database storage. Problems encountered with ceramic material classification tables derived from a draft VAMAS document have been alleviated due to a major revision of that draft document and its adoption by ASTM Committee C-28 on Advanced Ceramics. The E-49 document has been revised as much as can be done outside of the task group meetings. Several negative votes need committee votes before the remaining changes can be made. Database personnel plan to attend the ASTM committee meetings in May 1994, in Montreal.

The database summary report for 1993 was completed, reviewed, revised, and published during this semiannual period.

Communications/visits/travel

None.

Problems encountered

None.

Status of milestones

On schedule.

Publications

The Ceramic Technology for Advanced Heat Engines Project Database: September 1993 Summary Report, ORNL/M-3155, has been published.

3.2 TIME-DEPENDENT BEHAVIOR

Fracture Behavior of Toughened Ceramics

H. T. Lin, P. F. Becher, and W. H. Warwick (Oak Ridge National Laboratory)

Objective /scope

Ceramics with reinforcing microstructures and ceramic composites offer important advantages for heat engine applications. Chief among these is the improved fracture toughness that can be achieved by appropriate design of microstructural and material parameters. Previous studies show that these materials often exhibit substantial improvement in damage, thermal shock, and slow crack growth resistances. However, design of such systems must also consider those factors influencing their performance at elevated temperatures.

In response to these needs, studies are conducted to determine the mechanical properties, (e.g., creep, delayed failure, strength, and toughness) at elevated temperatures for these toughened ceramics. Particular emphasis is placed on understanding how microstructure and composition influence the mechanical performance at elevated temperatures and the stability of these properties for extended periods at these temperatures. The knowledge gained from these studies provides input on how to modify materials to optimize their mechanical properties for the temperature ranges of interest.

Technical highlights

During this 6-month reporting period, research efforts were directed at (1) characterization of the strength and toughness behavior of gas-pressure-sintered (GPS) silicon nitride ceramics and (2) evaluation of creep behavior of the reaction-bonded silicon nitride (SRBSN) ceramics. These are part of a large effort to provide an understanding of the influences of microstructure and composition on the creep behavior of self-reinforced Si_3N_4 ceramics with elongated grain microstructure and to develop more cost-effective approaches to manufacture Si_3N_4 materials.

1. GPS silicon nitride ceramics

Studies of the effect of secondary phases on the strength and toughness behavior of GPS Si_3N_4 ceramics were conducted in this reporting period. The GPS process was employed to grow highly developed elongated grain structures and to obtain high-toughness silicon nitride ceramics with refractory secondary phase(s).^{1,2} The GPS Si_3N_4 ceramics with rare-earth apatites were fabricated under W.B.S. Element 1.2.3.1 (Dispersion-Toughened Ceramic Composite). The rare-earth apatite grain boundary phases in these Si_3N_4 ceramics are $\text{Sr}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ (TRSN28), $\text{Mg}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ (TRSN29), and $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (TRSN30). The Si_3N_4 materials were GPS to >98% theoretical density with a two-stage cycle furnace run; 1900°C for 2 h and 0.6 MPa followed by 1950°C for 1 h and 2 MPa. A post-heat treatment at 1400°C for 1 h was

then performed to crystallize the apatite phase, which was consequently confirmed by X-ray analysis. The scanning electron microscopy analysis of plasma-etched surfaces of these GPS Si_3N_4 materials revealed that the elongated microstructure is quite similar in each composition.

The flexural strength in 4-point bending (6.4-mm inner span versus 19-mm outer span) was characterized at temperatures from 20 to 1370°C in air under a loading rate of approximately 100 MPa/s. In addition, the toughness behavior at room temperature was characterized by using a multiple indentation and fracture method (controlled-flaw technique).³ Indentation loads ranging from 9.8 to 490 N were employed in order to determine the R-curve response. The indented bend bars were fractured in 4-point bending (6.4-mm inner span versus 19-mm outer span) at a crosshead speed of 0.51 mm/min. Three specimens were tested at each indentation load.

Figure 1 shows the strength results as a function of temperature for GPS Si_3N_4 ceramics with various rare-earth apatite grain boundary phases (TRSN28, 29, and 30). The strength result of GPS AY6 material (TRSN1-2) is used as a baseline for comparison. The grain boundary phase in TRSN1-2 is amorphous. The results show that room-temperature strengths of these GPS Si_3N_4 materials are not sensitive to the apatite phases present and are low compared to other advanced Si_3N_4 materials.⁴ The observed low flexural strengths are due to the presence of hard agglomerates formed during the green-forming processes.⁵ The strength versus temperature data indicate that the materials containing apatite phases of La-Sr and La-Mg retain ~75% of their flexural strength at 1200°C, while materials with Sr-La-Yb-apatite and AY6 retain ~65% of their strength. In addition, materials with La-Sr and La-Mg apatites exhibit a substantial degradation in strength (~50%) at temperatures up to 1370°C. On the other hand, the strength of Sr-La-Yb-apatite material still remains about constant (~340 MPa) at temperatures between 1200 and 1370°C. The similarity in strength degradation between these apatite-containing GPS Si_3N_4 ceramic materials and AY6 material at elevated temperatures suggests that the apatite phases investigated in this study may not be suitable for high-temperature application.

Figure 2 shows the toughness versus crack length data for GPS Si_3N_4 materials containing apatite phases of La-Sr and La-Mg and material with AY6 additive. The results indicate that the La-Sr-apatite material has a higher steady-state toughness value (8.5 $\text{MPa}\sqrt{\text{m}}$) than the La-Mg-apatite material (7.0 $\text{MPa}\sqrt{\text{m}}$), but the degree of R-curve response (the rate of rise of fracture resistance with crack length) is insensitive to the apatite phases present. The data also show that the apatite-containing materials exhibit a relatively poor R-curve response (slow rise of R-curve with initial extension of crack length) and low steady-state toughness value as compared to AY6 materials. The similar R-curve response observed in apatite-containing materials may arise from the similarities in thermomechanical properties of apatite phases and/or bonding between apatite and $\beta\text{-Si}_3\text{N}_4$ grain.

2. SRBSN

Flexural creep studies of the SRBSN were part of the major efforts in this reporting period. The objective of this study is to evaluate the influences of microstructure, Si powder purity, and the processing method (microwave versus

Fig. 1 Flexural strength versus temperature curves for gas-pressure-sintered silicon nitride ceramics containing rare-earth apatite phases.

Fig. 2. Fracture resistance versus crack length curves for gas-pressure-sintered silicon nitride ceramics containing rare-earth apatite phases.

conventional heating process) on the creep behavior of SRBSN materials. The SRBSN materials were fabricated under W.B.S. Element 1.1.2.4 (Microwave Sintering of Silicon Nitride). This is part of a large effort to develop more cost-effective approaches to fabricate silicon nitride ceramic components and to assess their application limits as structural materials.

The starting powders for both microwave-SRBSN (MW-SRBSN) and SRBSN fabricated by conventional process (designated as TM145X and TM145Z, respectively) consisted of metallurgical grade Si (<0.5 wt % impurities, Elkem Metals Co.); α - Si_3N_4 (Stark Grade LC-10N); and oxide additives.⁶ An SRBSN material (TM142) containing Si powder with higher purity (<0.05 wt % impurities, Elkem Metals Co.) was also fabricated by microwave process to evaluate the effect of powder purity on creep rate. The nominal composition of TM145 and TM142 materials after nitridation and sintering is Si_3N_4 -3 wt % Al_2O_3 -9 wt % Y_2O_3 . The conventional processing for the SRBSN material (TM145Z) was conducted in a graphite-resistance heated furnace in a two-step process.⁶ The X-ray analysis indicates that the TM145X (and Z) and TM142 materials contain 100% β - Si_3N_4 plus a grain boundary glassy phase. The flexural strength results at room temperature also show that TM145X exhibits higher strength (744 MPa) as compared to TM145Z (600 MPa) or TM142 (687 MPa). The densities of these SRBSN materials are ~ 97 to 98% of the theoretical density of Si_3N_4 .

Figure 3 shows the flexural creep results of MW-SRBSN and SRBSN (TM145X and TM145Z) at 1200°C and at stresses from 100 to 250 MPa in air. The creep results were obtained from single-stress or sequential multiple-stress tests. Results from the single-stress test indicate that the MW-SRBSN (TM145X) exhibits much better creep resistance at 1200°C than the SRBSN (TM145Z). The threshold stress above which the MW-SRBSN (TM145X) exhibits a high creep rate (short creep life) is ~175 MPa, whereas the threshold stress for SRBSN (TM145Z) is ~100 MPa. The TM145X exhibits creep rates that are approximately two orders of magnitude lower than TM145Z at stress levels between 75 and 175 MPa. On the other hand, the creep data obtained under sequential multiple-stresses, starting at a stress less than threshold stress, show that both TM145X and TM145Z exhibit similar creep rates and stress exponent ($n \sim 1$) under the stress ranges employed. A creep stress exponent (n) of one is generally attributed to diffusional or viscous creep processes. The creep results of MW-SRBSN materials as a function of Si powder purity at 1200 and 1250°C are illustrated in Fig. 4. The results indicate that the material (TM142) fabricated with higher purity Si powder exhibits relatively low creep rates (about twofold) with respect to that of TM145X made with lower purity Si powder under the test conditions employed. In addition, the stress exponent of both materials is also approximately one.

The difference in the creep resistance at elevated temperatures between TM145X and TM145Z may arise from the differences in elongated grain microstructure and/or pore morphology. It is noted that the MW-SRBSN has a microstructure that exhibits a larger number density of large, highly developed elongated grains with higher aspect ratio (~ 6 to 9) than that developed in the SRBSN (aspect ratio ~ 3 to 5). As a result, TM145 X has a higher fracture toughness (~ 7.7 $\text{MPa}\sqrt{\text{m}}$) as compared to that of TM145Z (5.3 $\text{MPa}\sqrt{\text{m}}$). The difference in pore morphology

Fig. 3. Strain rate versus stress curves for microwave and conventional sintered reaction-bonded silicon nitride ceramics.

Fig. 4. Strain rate versus stress curves for microwave-sintered reaction-bonded Si_3N_4 ceramics as a function of Si purity.

(size and distribution) could also lead to a different oxidation rate and oxidation-induced damage resulting in a different creep response. A companion creep test was conducted on the specimens that were thermally annealed at 1200°C for 120 h in air to seal the pores present on the tensile surface. The preliminary results indicate that the pre-oxidized specimens tested at stresses above threshold stress exhibit similar creep rates as those obtained under the stepwise-stress condition without pre-oxidation treatment; see Fig. 3. On the other hand, the presence of more impurities (i.e., Fe) will lead to a less refractory secondary phase lowering the creep resistance of Si_3N_4 . The greater creep resistance observed for MW-SRBSN using high purity Si-powder (TM142) is also reflected in its greater retention of flexural strength (~85%) at temperatures up to 1000°C in air.⁶

Status of milestones

Milestone No. 321316: "Characterization of flexural creep behavior of microwave-sintered reaction-bonded Si_3N_4 ceramics" was completed.

Milestone No. 321317: Complete evaluation of static fatigue and creep behavior of GPS Si_3N_4 ceramics will be delayed until October 1994, due to the delay in receipt of materials from W.B.S. Element 1.2.3.1. (Dispersion-Toughened Ceramic Composite).

Publications

None.

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Cyclic Fatigue of Toughened Ceramics

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Objective/scope

The objective of this task is multifold:

1. To develop, design, fabricate, and demonstrate the capability of performing cyclic fatigue in tension-tension/compression and static fatigue testing in uniaxial tension/compression on candidate structural ceramics at elevated temperatures. While significant progress has been made in several areas of the experimental front (such as specimen/grip alignment, specimen heating, and high-temperature extensometry), testing capabilities in fully reversed tension-compression cyclic fatigue and compression creep in the uniaxial direction remain to be developed and demonstrated.
2. To develop baseline information on cyclic fatigue behavior of candidate ceramics and, in turn, to establish a design data base.
3. To develop creep and creep-rupture data bases for advanced heat-engines design applications in the 1150 to 1370°C range.
4. To evaluate and refine existing constitutive models based on the information generated above.
5. To develop new constitutive models to facilitate design analyses of high-temperature structural components and improve their reliability.

Technical highlights

Tension/Compression Cyclic Fatigue Testing

The electrohydraulic universal testing machine has been checked out for fully reversible cyclic fatigue testing and is operational except for a minor glitch in the specimen gripping heads that is being fixed by the supplier. The gripping heads have been aligned and checked with a strain-gaged specimen, showing the maximum bending occurring in the gage section is about 3%. An estimation indicates that the inherent misalignment falls within the machining tolerance.

An aluminum dummy specimen was successfully cycled in tension and compression for about 100 h without buckling. However, the final alignment check will not be completed until a successful cyclic fatigue test at high temperature of a ceramic specimen can be conducted. Four buttonheadless ceramic specimens have been fabricated from a GN-10 tile, and preliminary testing will begin as soon as the heating system can be made operational.

The specimen will be heated indirectly by an induction coil via an SiC susceptor, but the heating configuration will be different from that now being used in cyclic fatigue testing due to the limited space between the gripping heads. This mode of heating is effective and ideal for heating a ceramic specimen in a confined space, as is the case here. An induction coil, an SiC susceptor, and heat-insulating holders have been fabricated and are being assembled for a trial.

A minor setback occurred during the dummy specimen testing due to a slow leakage of hydraulic oil through the oil pressure regulator. This, in turn, caused a gradual loss of hydraulic gripping power in the heads. Although the slow oil leakage did not

cause the specimen to slip out of the gripping heads, it must be fixed for long-term testing. The problem is currently being corrected by the supplier.

Cyclic Fatigue of $\text{SiC}_w/\text{Al}_2\text{O}_3$ (CERCOM PAD-AS34W)

Previously, we showed that whisker reinforcement can enhance the tensile strength as well as cyclic fatigue resistance of monolithic Al_2O_3 , but the strengthening effects diminished as temperature increased to 1200°C. Test results obtained at elevated temperatures showed that the enhanced resistance to fatigue degenerated somewhat at 1000°C and was lost entirely at 1200°C.

To fill the information gap, several cyclic fatigue tests were performed at 1100°C. A triangular wave form shown in Fig. 1(a) was used. Test parameters and test results are summarized in Table 1, and data (triangular symbols) are plotted in Fig. 2. The open triangle attached with an arrow indicates that the test condition was changed at the number of cycles indicated when the peak stress amplitude was increased to the next higher level, as shown in Fig. 1(b), and no specimen failure had occurred. Therefore, the open data points are interconnected by broken lines to symbolize that a common specimen was used. When the peak cyclic amplitude was increased to the next higher level with no specimen failure, the specimen was considered undamaged by fatigue; therefore, the lifetime was recounted and plotted as that for a virgin specimen. Each of the filled triangles indicates a specimen failure, but the one with an arrow indicates that the test was terminated by an unexpected disruption such as a power outage. The arrow implies that the cyclic fatigue life would have been longer if the premature failure had not occurred.

The fatigue curve of $\text{SiC}_w/\text{Al}_2\text{O}_3$ at 1100°C was not determined due to the data scatter and the limited number of test results. It should be noted that the best fatigue performance was given by a specimen made from stock tile No. 1, and low-fatigue performances were given by those made from tile No. 3, as noted in Table 1. This observation may indicate that the inconsistency in fatigue performance is caused by the nonuniformity in commercial grades of ceramic materials. A general observation indicates that the fatigue property of this composite material at 1100°C may be about the same or below that of unreinforced monolithic Al_2O_3 at room temperature.

Detection of Acoustic Emission (AE) Signals in Cyclic Fatigue of Ceramics at High Temperature by Wave Guide

An exploratory study was conducted to detect AE signals in cyclic fatigue of ceramic materials at high temperature, using wave guides as an intermediate between the hot test specimen and the AE sensors. This study was performed concurrently during the recent fatigue testing discussed above. AE signals were detected while $\text{SiC}_w/\text{Al}_2\text{O}_3$ specimens were being cycled at 1100°C.

Since this was the first exploratory experiment, a number of valuable experiences and new insights uniquely associated with AE detection at high temperature were gained. For example, setting the optimum values of all AE parameters that control the signal measurement process must be experimentally determined by trial and error, because the control values used previously for room-temperature AE detection were invalidated not only by temperature but also by the introduction of the waveguide. In a fatigue test, the AE detection system was either overwhelmed by a flood of signals due to setting the threshold amplitude too low or conversely missing useful signals by setting the limiting

- (a) Wave Form I:
Constant Amplitude Loading
 $R = \text{min./max. stress} = 0.1$

- (b) Wave Form II:
Increasing Multiple-Step Loading

Fig. 1. Wave forms used in cyclic fatigue tests.

Table 1. Results of cyclic fatigue tests on SiC whisker-reinforced Al_2O_3 tested at 1100°C.

Specimen number	Loading sequence	Cyclic stress (MPa)	Number of cycles at intermediate loading	Number of cycles to failure
1-9 ^a	1	220	734,084	
	2	240	1,350,011	
	3	255	20,815	2,104,910
3-1	1	250		1,360
3-2	1	225		223
3-3	1	200		2,156
3-5	1	180		5,050
3-6	1	160		999

^aThe first number designates stock tile number.

Fig. 2. Comparisons of cyclic fatigue behavior of monolithic Al_2O_3 and SiC whisker-reinforced Al_2O_3 matrix composite materials tested at room and elevated temperatures.

variable too high. After a number of iterative exercises, a set of appropriate values for the AE parameters can be determined for a particular specimen. However, the AE control parameters did not uniformly apply to other specimens even though the specimen material was the same.

The disparity in volume of AE signals detected from the two extensometer probes used as waveguides remained a problem, which tended to obscure the interpretation of the data. Currently, the AE sensors are situated on the far end of the extension rods, which are composed of three different materials. It has been suggested that using a monolithic ceramic rod as a waveguide may mitigate the problem. An attempt is being made to erect an independent fixture for new waveguides.

Creep Testing of NT-154 Si_3N_4

Three ongoing creep tests on NT-154 have been performing well in spite of brief interruptions that occurred recently to two of the tests due to the failure of heating elements. The status is as follows:

Specimen 20-56 (see Fig. 3): The test has been interrupted recently due to a furnace power failure. Reheating and reloading the specimen to the original test condition at $1250^\circ/175$ MPa did not appear to have altered the creep behavior showing before the test was interrupted. Perhaps, this is the longest creep test for this material ever recorded, completing nearly 2.8 years (24,330 h) of testing. The test is continuing with a creep rate of $\sim 2.13 \times 10^{-11} \text{ s}^{-1}$, reasonably steady for the last 10,000 h, and a total of 0.9% creep strain accumulated to date. The creep curve shows that primary creep was very extensive for the specimen, which began to show a credible sign of steady-state creep only after 15,000 h of testing. This observation suggests that short-term test data can not provide complete data information to implement a safe and sound structural design practice.

Specimen 20-00 (see Fig. 4): The test is continuing at 1250°C under a constant stress of 150 MPa. The specimen has accumulated a total of 0.55% strain after about 21,000 h (~ 2.4 years) of testing. The average creep rate was determined from the last 10,000 h of the creep curve to be $\sim 2.5 \times 10^{-11} \text{ s}^{-1}$.

Specimen 20-32 (see Fig. 5): The specimen has been tested at 1250°C under a constant stress of 150 MPa for about 14,500 h since the stress was reduced from the earlier testing condition at 175 MPa. The test was briefly interrupted recently due to the failure of heating elements. Immediately following the full reloading to the original test condition, pronounced transient creep that occurred in the first reloading at $t = 2400$ h but not in other occasions (as seen in Fig. 5) was discerned. However, the creep rate decreased to about the same rate occurring prior to the test was interrupted. The creep rate is about the same as that of specimen 20-00 currently being tested at the same condition.

Creep Testing of GN-10 Si_3N_4

The status of three ongoing creep tests on GN-10 Si_3N_4 at the low-stress end of the creep-rupture range (long-term tests) is as follows:

Specimen 89367-1-2 (see Fig. 6): The specimen has been tested at 1200°C and 125 MPa for 9400 h (>1 year) with a total creep strain of 0.65%, and the test is continuing. The erratic creep behavior, as exemplified by intermittent strain riser and

Fig. 3. Creep curve of NT-154 Si_3N_4 (specimen 20-56) tested at 1250°C and 175 MPa. No indication of imminent failure has been observed after nearly three years of testing.

Fig. 4. Creep curve of NT-154 Si_3N_4 (specimen 20-00) tested at 1250°C and 150 MPa. The average creep rate was determined from the last 10,000 h of the creep curve to be $\sim 2.5 \times 10^{-11} \text{ s}^{-1}$.

ORNL-DWG 92-14551R3

Fig. 5. Creep curve of NT-154 Si₃N₄ (specimen 20-32) tested at 1250°C under step-down loading conditions as indicated. Pronounced transient creep occurred following the most recent test interruption at $t = \sim 16,240$ h by the failure of heating elements. However, the transient creep settled down rather quickly to the same level occurring prior to the test being interrupted.

ORNL-DWG 93-8286R3

Fig. 6. Creep curve of GN-10 Si₃N₄ (specimen 89367-1-2) tested at 1200°C with an applied stress of 125 MPa. The erratic creep behavior, as exemplified by intermittent strain riser and recovery, has gradually subsided to a reasonably stable level.

recovery periods reported previously, has gradually subsided to a reasonably stable level. Therefore, the general trend of the creep behavior is now definable, showing that the creep rate has increased somewhat during the last 1500 h of testing in the tertiary creep regime.

Specimen 89367-1-3 (see Fig. 7): This specimen has been tested at 1150°C and 150 MPa for 10,000 h (>1.1 year) of testing. The creep behavior continued to be very erratic, despite the fact that the specimen has gone through a long period of testing in excess of 1 year. A sharp decrease in creep strain was observed beginning at $t = \sim 8200$ h for unknown reasons prior to an unscheduled shutdown due to the loss of furnace power. Subsequently, the system was restored to the original test condition, but the creep strain continued to decrease initially until it stabilized with a net loss of about ~ 700 microstrain below the peak strain amplitude. The extensometer was inspected and calibrated during the brief period of the shutdown, but results of the careful investigation revealed no suspicious origins of the negative creep strain. Since a smooth creep curve was obtained for a previous test with an applied stress of 200 MPa, which is higher than this case by 50 MPa, it appears that this erratic behavior may be inherent to GN-10 when tests are done below certain combined test conditions of temperature and stress.

Specimen GCC-14 (see Fig. 8): This specimen ruptured after completing 5547 h of testing at 1260°C with an applied stress of 80 MPa. The specimen has accumulated a total creep strain of 3.26%. The creep curve shows extensive primary creep and a period of steady state creep occurring between $t = 3000$ to 5000 h, followed by a hint of tertiary creep occurring subsequently until specimen rupture.

Creep Testing of CERCOM $\text{SiC}_w/\text{Al}_2\text{O}_3$ at 1000°C

Specimen 4-7 (see Fig. 9): This specimen has been tested with an applied stress of 50 MPa for about 3500 h, and the test is continuing with extensive steady state creep at a rate of $\sim 2 \times 10^{-13} \text{ s}^{-1}$ during the last 3000 h of testing.

Specimen 3-5 (see Fig. 10): This test has been completed after 1258 h of testing with an applied stress of 90 MPa. Results are compared with those obtained from two previous tests each at 75 and 100 MPa. The latter test ended in less than 30 h, being suspected to have failed prematurely, while the former lasted for nearly 700 h. This test was intended to fill in the information gap between the two earlier tests. However, the creep curve of the 90-MPa test was inconsistent in the sense that it did not fall between the 75- and 100-MPa creep curves. Such inconsistency is not unusual if specimens are made from different stock tiles, which are identified by the first of the hyphenated specimen numbers.

Creep Testing of Microwave-Annealed GS-44 Si_3N_4

Exploratory creep testing has been initiated following receipt of 15 specimens fabricated from the 3 experimental tiles, each having been microwave annealed at 1400, 1500, and 1600°C for 10 h.

Since no information is available concerning the creep behavior of this material, a specimen annealed at 1400°C was tested at 1000°C with an applied stress of 160 MPa as a starting point for preliminary scoping studies. Test results obtained to date are compared with the creep curve of microwave-annealed SNW-1000 Si_3N_4 (annealed at 1400°C for 20 h) tested in the same condition, as shown in Fig. 11. Results of initial 500 h show

Fig. 7. Creep curve of GN-10 Si_3N_4 (specimen 89367-1-3) tested at 1150°C with an applied stress of 150 MPa. The creep behavior continued to be erratic during the last 1000 h of testing. The cause of the negative creep strain occurring at $\approx \sim 9200$ to 9300 h is not known. Results of careful inspection and calibration of the extensometer revealed no clues.

Fig. 8. Creep curve of GN-10 Si_3N_4 (specimen GCC-14) tested at 1260°C with an applied stress of 80 MPa. The creep curve exhibited extensive primary creep with a hint of tertiary creep occurring during the last 700 h of testing prior to fracture.

Fig. 9. Creep curve of SiC whisker-reinforced Al₂O₃ (specimen 4-7) tested at 1000°C and 50 MPa. The test is continuing with an extensive steady state creep at a rate of $\sim 2 \times 10^{-13} \text{ s}^{-1}$.

Fig. 10. Comparison of creep curves for SiC_(w)/Al₂O₃ tested at 1000°C under various loads as indicated. The inconsistency in creep behavior exhibited by the specimen tested with 90 MPa is probably due to the lot variation.

Fig. 11. Comparison of creep curves for GS-44 and SNW-1000 Si_3N_4 tested at 1000°C and 160 MPa. Both specimens were annealed at 1400°C, 10 h for GS-44 and 20 h for SNW-1000.

that the creep resistance of GS-44 is superior to that of SNW-1000 by a factor of ~ 14 in terms of creep rate, and by a factor of at least 10 in terms of total accumulative creep strain.

Tensile-Rupture Testing of NT-154 Si_3N_4 in Support of the ATTAP Program

Phase 1 task effort was completed in 1993, and Phase 2 continued. The current test matrix identifies 40 tests to be completed in the temperature range of 982 to 1315°C and stress ranges that yield time to failure up to 500 h.

The status and progress of this task effort are summarized in Table 2. Six of the eight exploratory tests were concluded with mixed success. All of the specimens initiated rupture from inclusions suspected to be of iron. As a result, four specimens failed far short of desired lifetimes. The sixth test (specimen 34711) was successfully completed with a rupture time of 761.2 h, which exceeded the estimated time to failure by 351 h. It is interesting to note that this specimen also failed from an internal inclusion having a size comparable to those observed in the contaminated specimens. Nevertheless, it did not fail in the same manner as fast fracture. The seventh test (specimen 34713) at 1315°C and 224 MPa also outlived the estimated time to failure, and the test is currently still in progress with no indication of imminent failure.

Table 2. Results of Stress-Rupture Tests for ATTAP Specimens

Specimen No.	Temp. °C/°F	Stress MPa / ksi	Desired time to failure h	Rupture time h	Remarks	Status ^a
34708	982 / 1800	466 / 67.5	1 - 150	<0.001	(1) Ruptured at 361 MPa before fully loaded to 466 MPa. (2) Failure initiated from an inclusion.	C
34709	1093 / 2000	431 / 62.5	1 - 150	4.2	Failure initiated from a large inclusion.	C
34712	1204 / 2200	328 / 47.5	150 - 300	<0.017	Rupture initiated from a large inclusion.	C
34707		" / "	"	1.27	Failed from a large inclusion.	C
34710	1260 / 2300	293 / 42.5	150 - 300	<0.001	(1) Ruptured at 274 MPa before fully loaded to 293 MPa (2) Failure initiated from a large inclusion	C
34711		" / "	"	761.2	(1) Exceeded estimated rupture time by 461 h. (2) Fracture initiated from an inclusion.	C
34713	1315 / 2400	224 / 32.5	150 - 300	>360	(1) Exceeded estimated rupture time. (2) Has completed 360 h of testing to date.	I/P

^aC indicates completion and I/P in progress.

Important Findings and Observations

Preliminary test results showed that microwave annealing can significantly increase the creep resistance of GS-44 Si_3N_4 more effectively compared to that done to SNW-1000 Si_3N_4 by an order of magnitude in terms of creep rate.

Status of milestones

Completed a technical report covering results of tests on $\text{SiC}_w/\text{Al}_2\text{O}_3$ ceramic composite at elevated temperatures (Milestone 321417, due on October 31, 1993).

Publications

1. J. L. Ding, K. C. Liu, and C. R. Brinkman, "A comparative Study of Existing and Newly Proposed Models for Creep Deformation and Life Prediction of Si_3N_4 ," *Life Prediction Methodologies and Data for Ceramic Materials, ASTM STP 1201*, ed. C. R. Brinkman and S. F. Duffy, American Society for Testing and Materials, Philadelphia, 1994.
2. J. L. Ding, K. C. Liu, K. L. More, and C. R. Brinkman, "Creep and Creep Rupture of an Advanced Silicon Nitride Ceramic," officially accepted for publication in J. Am. Ceram. Soc.

Rotor Data Base Generation

A. A. Wereszczak, T. P. Kirkland, H. Cai, and
M. K. Ferber (Oak Ridge National Laboratory)

Objective/scope

There are three central goals of the proposed research program. High-temperature mechanical testing, microstructural characterization of failure phenomena, and the modeling of high-temperature deformation in candidate silicon nitrides are under investigation. The fundamental understanding of the evolution of damage, and ultimately the high-temperature mechanical performance and service life, is information that is critical for the progress toward implementation of structural ceramics as components in internal combustion and automotive gas turbine engines.

The systematic study of the high-temperature mechanical performance of silicon nitride is undertaken as a function of temperature and time. Two temperature regimes will serve as an independent parameter: $T \approx <1000^{\circ}\text{C}$ and $T \approx >1000^{\circ}\text{C}$, which are desired operating temperature ranges for internal combustion and automotive gas turbine engines, respectively. Tensile stress-rupture data will be generated by measuring fatigue life at a constant or cyclic stress. The time-dependent deformation will also be monitored during testing so that the extent of high-temperature creep may be ascertained.

The second goal is to characterize and understand the evolution and role of damage mechanisms associated with high-temperature deformation in silicon nitride. Tested specimens will be characterized using established ceramographic, scanning electron microscopy (SEM), TEM, and non-destructive acoustic techniques. Microstructural aspects of high-temperature failure will be examined and include:

- (1) extent of slow crack growth,
- (2) evolution of cavitation-induced damage and fracture,
- (3) transition between brittle crack extension and cavitation-induced growth,
- (4) crack blunting, and
- (5) the evolution and role of oxidation-assisted damage.

As the third goal, the resulting stress-rupture data will be used to examine the applicability of a generalized fatigue-life (slow crack growth) and creep model. Refinements will be implemented to account for the damage mechanisms listed. Consequently, the data generated in this program will not only provide a critically needed base for component utilization in internal combustion and automotive gas turbine engines, but also facilitate the development of a design methodology for high-temperature structural ceramics.

Technical progress

In the previous reporting period, a test matrix was described that will be used to evaluate the high-temperature mechanical performance of a commercially available, yttria-fluxed, hot isostatically pressed (HIPed) silicon nitride (NCX-5102, Saint-Gobain/Norton Industrial Ceramics Corp., Northboro, Massachusetts). The

test matrix was chosen to facilitate the understanding of the microstructural aspects of high-temperature failure listed above in the scope of the project. The elevated-temperature testing includes tension static and cyclic testing in ambient air and inert environments.

The deleterious effects of "spotting" in NCX-5102 silicon nitride were previously described [1]. Button-head tensile specimens of NCX-5102 containing these "spots" do not mechanically perform at high temperatures as well as specimens with no spots. A collaborative effort with Saint-Gobain/Norton Industrial Ceramics Corporation to further explore the mechanisms associated with "spots" in NCX-5102 is under way. A 20-specimen test matrix will be examined which will systematically compare "spotted" and "unspotted" NCX-5102. Ten different high-temperature test conditions (a spotted + unspotted specimen per condition) will involve static creep testing in inert and ambient environments.

Strain histories of tested NCX-5102 button-head specimens are summarized in Figs. 1 and 2. The strain-time plots in these two graphs show that the spotted NCX-5102 specimens creep faster under static conditions than unspotted ones and that cyclic loading results in less overall creep and longer lifetimes. A similar trend was observed in another HIPed silicon nitride (PY6, GTE Laboratories, Waltham, Massachusetts); a trend that has been the subject of several publications [2-5]. The tensile strain as a function of time for two specimens each at 1260 and 1370°C subjected to 0.1-Hz, triangular waveform, tension-tension cyclic loading is shown in these two figures. The specimens appear to be exhibiting steady state creep, which is different than the transient nature of the creep curves for the specimens that were statically loaded. The minimum strain rate as a function of stress for these test cases is shown in Fig. 3. The data interpretation; microstructural analysis; and comparison of static, dynamic, and cyclic performances are being used to further explore the evolution of the damage mechanisms. It has been suspected that the viscoelastic nature of the grain boundary phase at elevated temperatures is manifesting itself somehow in the longer lifetimes. The viscoelastic component of creep is being further examined with the NCX-5102 silicon nitride at 1260 and 1370°C.

During the present reporting period, high-temperature tension-compression cyclic fatigue testing was initiated on NCX-5102 silicon nitride. The specimen is held in fixed grips on a servo-hydraulic testing machine. The minimization of axial and concentric bending at the maximum tensile and compressive stress was required prior to the initiation of the test. The specimen is heated in a short furnace that: is mounted on the testing machine, is positioned between the two grips, and is capable of generating 1500°C. The evolution of high-temperature-associated damage in tension-compression cyclic fatigue is being investigated and compared with that of specimens tested in static and tension-tension cyclic fatigue. For the first test, a sinusoidal waveform was chosen

(1 Hz), and the specimen was stressed to ± 220 MPa at 1260°C. The test was interrupted after 3.7 million cycles, and the residual room-temperature tensile strength was 635 MPa. This is less than the 1 GPa room-temperature tensile strength advertised by the manufacturer. Fractography showed that the specimen failed via fast fracture from an intrinsic defect. If damage was generated during the tension-compression cyclic test at 1260°C, then it was not the source of the

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Fig. 1. Strain histories as a function of time at 1260°C for spotted (S) and unspotted (U) NCX-5102 subjected to static and cyclic loadings.

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Fig. 2. Strain histories as a function of time at 1370°C for spotted (S) and unspotted (U) NCX-5102 subjected to static and cyclic loadings.

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Fig. 3. Minimum strain rate as a function of stress at 1260°C (top) and 1370°C (bottom) for NCX-5102. Note: U = unspotted, S = spotted.

room-temperature fracture. Lenticular cavities were not observed when the fracture surface microstructure was examined using SEM.

To examine the viscoelastic effect of the grain boundary phase in the NCX-5102 silicon nitride, creep recovery (strain relaxation-constant stress after unloading) and stress relaxation (constant strain) tests have been initiated. By jointly examining the strain and stress relaxation behavior of this material at elevated temperatures, the contribution of viscoelastic or anelastic strain in static and cyclic loading may be examined. The testing machine being utilized for this examination (Instron 1380) is capable of operating in load or strain control (with contact extensometry) via electronic closed-loop control. The motivation is to examine the stress and strain relaxation times and determine if/how they can affect the cyclic fatigue performance of the same material. Figure 4 shows an example of strain relaxation for an NCX-5102 specimen after the stress had been reduced to 70 from 140 MPa at 1370°C. The total recovery is comprised of elastic and viscoelastic strain with the unrecoverable strain being plastic in nature. By varying the unloading stress, the functionality of viscoelastic strain (linear or nonlinear) can be identified.

Several creep-recovery studies have been completed and two interesting observations have been made that are warranting further examination: (1) the viscoelastic component is a small fraction of the total strain in PY6 and NCX-5102 silicon nitride[6], and (2) the plastic component of creep is not linear with time. A mathematical representation of creep, described in a previous bimonthly [7] that stems from work of Pao and Marin[8], represents the plastic component of the total creep as a linear function of time (i.e., "steady state" creep). However, when the elastic and viscoelastic components of creep were subtracted from the measured total creep strain, the remaining plastic component of creep was not linear as shown in Fig. 5. The time-exponent of the plastic strain component was found to range between 0.4 to 0.6 (it would equal 1 for true steady state) for the creep recovery tests examined to date.

The stress relaxation experiment involves stressing a button-head tensile specimen under load control, then transferring to strain control to maintain a constant strain. The relaxation of stress is then monitored as a function of time. The total strain (ϵ_{tot}) may be represented as the sum of the elastic (ϵ_{el}), viscoelastic, and plastic strains. The sum of viscoelastic and plastic strains can be grouped into one parameter described as the inelastic strain (ϵ_{in}). Consequently, the total strain is

$$\epsilon_{tot} = \epsilon_{el} + \epsilon_{in} \quad (1)$$

Similarly, the time derivative of each component is related according to

$$\dot{\epsilon}_{tot} = \dot{\epsilon}_{el} + \dot{\epsilon}_{in} \quad (2)$$

A stress relaxation test maintains ϵ_{tot} constant, so $\dot{\epsilon}_{tot} = 0$. The elastic strain rate is equal to $\dot{\sigma}/E$, where $\dot{\sigma}$ is the instantaneous stressing rate and E is

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Fig. 4. An example of creep recovery (strain relaxation) on NCX-5102 at 1370°C in ambient air.

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Fig. 5. The total creep strain may be broken into its three separate components once creep recovery tests have been conducted and the viscoelastic component has been identified.

Young's Modulus. The inelastic strain rate is then represented by

$$\dot{\epsilon}_{in} = -\dot{\sigma}/E \quad (3)$$

An example of a stress relaxation test is shown in Fig. 6. A comparison of strain rate as a function of applied stress for data generated at 1370°C with NCX-5102 silicon nitride from two static creep tests and one stress relaxation test is shown in Fig. 7. The two static creep tests were tested at 125 and 140 MPa. The creep rates from those two specimens were determined at test commencement (maximum strain rate), when a total of 2810 $\mu\epsilon$ had accumulated, and at specimen failure (minimum strain rate); neither of the creep histories from these specimens ever reached steady state, nor exhibited tertiary creep. The data from the relaxation test were generated when the specimen had accumulated 2810 $\mu\epsilon$; this is the reason behind the inclusion of the creep rates for the two static tests at 2810 $\mu\epsilon$. The data generated from the stress relaxation test are situated in the range between the minimum and maximum strain rates. Further exploratory studies of this technique and its validity are under investigation. The advantage of a stress relaxation test is that several decades of creep rates are transversed in several hours of experimentation with one specimen, whereas equivalent generated data using static creep tests require numerous specimens (one stress-strain rate data point per specimen) tested over a range of applied stresses.

Since the last reporting period, the development of a nondestructive technique was initiated to provide a tool that could conceivably identify the extent of damage in a crept structural specimen or component. Accumulated damage in the form of creep or slow crack growth ultimately leads to a time-dependent failure. Considerable effort has been given to the inclusion of time-dependent effects into existing probabilistic design methodology. However, the verification of these design methodologies is limited by the lack of appropriate tools for the non-destructive assessment of component damage.

The feasibility of acoustic resonance spectroscopy (ARS) as a nondestructive technique to evaluate such damage is being explored. ARS is based on the principle that the mechanical resonance of a component is a function of its shape, density, elastic moduli and defects in a sufficiently complex manner, such that a measurement of the resonant frequencies provides a unique signature of the component. A major advantage of the ARS technique is its high sensitivity. Changes in the shape, density, elastic moduli, or introduction of defects lead to a variation of this signature. The resonance spectrum is generated by sweeping the frequency of an acoustic signal applied to the component, and by detecting the resonant frequencies of the component.

In preliminary experiments, specimens of creep-tested PY6 silicon nitride were machined into rectangular parallelepipeds with nominal sides of 3 mm. The ARS test was conducted by holding a specimen by two opposite vertexes between two disc transducers. Resonant spectra were obtained for each specimen, and the shifts of selected resonant frequencies were studied as a function of creep strain. The results are summarized in Fig. 8. The results show a definite correlation between the frequency shift and the creep strain which demonstrates the feasibility of using ARS for characterizing creep damage. These results have provided

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Fig. 6. An example of stress relaxation on NCX-5102 at 1370°C in ambient air.

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Fig. 7. Stress-strain rate data generated with a single stress relaxation specimen compared with data from two static creep tests.

Fig. 8. The shift in frequency, as detected by ARS, exploits trends in creep strain in crept PY6 silicon nitride.

incentive to further explore the feasibility of ARS to detect cracks arising from subcritical crack growth or machining damage. If the detection of these types of cracks is successful, then the acoustic resonance spectroscopy may become a very useful nondestructive tool both for the verification of design methodologies and the inspection of finished ceramic engine components.

Status of milestones

A paper, entitled "Stress and Strain Relaxation Behavior in HIPed Silicon Nitrides," by A. A. Wereszczak, T. P. Kirkland, and M. K. Ferber was submitted for publication in *J. Mater. Sci. Lett.*

The submittal deadline for the final report on rotor data base generation for PY6 silicon nitride material was extended from June to December 1994.

Communications/visitors/travel

A. A. Wereszczak attended the 184th Meeting of the Electrochemical Society, New Orleans, Louisiana, October 11-12, 1993, and gave a presentation.

A. A. Wereszczak and T. P. Kirkland attended the 18th Annual Conference on Composites and Advanced Ceramic Materials, Cocoa Beach, Florida, January 10-14, 1994, and presented a paper and poster, respectively.

A. A. Wereszczak, H. Cai, and M. K. Ferber gave presentations at the 96th Annual Meeting and Exposition of the American Ceramic Society in Indianapolis, Indiana, April 24-27, 1994.

Problems encountered

None.

Publications

"Environmental Effects on the Flexure Strength of HIPed Silicon Nitride at Elevated Temperatures," A. A. Wereszczak, K. Breder, M. K. Ferber, T. P. Kirkland, and P. K. Khandelwal, pp. 686-87 in Extended Abstracts, Vol. 93-2, Fall Meeting of the Electrochemical Society, Electrochemical Society, Pennington, N.J., 1993.

"Role of Oxidation in Time-Dependent Failure Behavior of HIPed Silicon Nitride at 1370°C," A. A. Wereszczak, K. Breder, and M. K. Ferber, *J. Am. Ceram. Soc.* **76** [11], 2919-22 (1993).

"Effects of Oxidation and Creep Damage Mechanisms on Creep Rupture Behavior in HIPed Silicon Nitrides," A. A. Wereszczak, M. K. Ferber, and T. P. Kirkland, to be published in *Proceedings of the 18th Annual Conference on Composites and Advanced Ceramics*, Vol. 15, No. 7-10, 1994.

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TOUGHENED CERAMICS LIFE PREDICTION

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Objective/Scope

The purpose of this research is to understand the room temperature and high temperature [$\leq 1370^{\circ}\text{C}$ (2500°F)] behavior of toughened ceramics as the basis for developing a life prediction methodology. A major objective is to understand the relationship between microstructure and mechanical behavior within the bounds of a limited number of materials. A second major objective is to determine the behavior as a function of time and temperature. Specifically, the room temperature and elevated strength and reliability, the fracture toughness, slow crack growth and the creep behavior will be determined for the as-manufactured material. The same properties will also be evaluated after long-time exposure to various high temperature isothermal and cyclic environments. These results will provide input for parallel materials development and design methodology programs. Resultant design codes will be verified.

Technical Highlights

The high temperature strength and slow crack growth behavior of a hot-pressed silicon nitride material (SNW 1000) fabricated by GTE was determined. Young's modulus, density and fracture toughness at room temperature were also determined. This paper reports the results of these tests with an emphasis on high temperature slow crack growth behavior of the material. Strength and dynamic fatigue testing were carried out with MOR bar specimens under flexure loading.

Experimental Procedures

The material used in this study was a hot-pressed silicon nitride fabricated by GTE (vintage 1981). The flexural test specimens were cut from disk specimens measuring 3.66 mm in thickness and 38.10 mm in diameter. The final dimensions of the flexural test specimens were 3.66 mm by 2.86 mm by 38 mm in width, height and length, respectively. All the disk specimens were first annealed at 1200°C in air for 10 h to stabilize the glass phase [1] and then machined into the flexural test specimens. All the flexural test specimens were annealed at 1200°C in air for 1 h in order to remove any spurious residual stress and damage due to machining.

Machining damage is not typically a problem for properly machined uniaxial specimens (e.g. according to ASTM C1161). However, for multiaxial specimens, the procedures sufficient for uniaxial specimens are not adequate, as significant damage exist parallel to the longitudinal direction [2]. This bias of a flaw population (e.g machining damage) in one orientation requires an anisotropic reliability [2] analysis instead of the more common isotropic analysis that assumes a random orientation and distribution of flaws. In order to obtain a random orientation of

flaws, uniaxially ground specimen can be annealed [2], as done in this work.

Young's modulus and Poisson's ratio of the material were evaluated at room temperature using an impulse excitation technique on a total of 24 specimens. Density was determined by using a bulk density measurement technique on 12 specimens. Room-temperature fracture toughness was determined by the single edge precracked beam (SEPB) method. Five specimens with acceptable crack configurations were tested.

The strengths of SNW 1000 silicon nitride were determined from room temperature to 1300°C in air. Strength testing was carried out using a SiC four-point flexure fixture with 15/30 mm spans at a loading rate of 2680 N/min in an electromechanical testing machine (Instron, Model 8562). Five specimens were used at each temperature from room temperature to 1260°C, and fifteen specimens were used at 1300°C.

Dynamic fatigue testing was used to determine fatigue (slow crack growth) behavior of the material at 1150, 1260 and 1300°C in air. The testing was conducted using the same fixture and the same testing machine used for the strength testing. Two loading rates of 2.68 and 2680 N/min, corresponding to stressing rates of 2 and 2000 MPa/min, were used at temperatures of 1150 and 1260°C with the tests at the fastest loading rate (2680 N/min) also serving to measure the strength. Five specimens were used at each loading rate. At 1300°C, three loading rates of 2.68, 85 and 2680 N/min, corresponding to the stressing rates of 2, 63, and 2000 MPa/min, were used. A total of fifteen specimens were used at each rate. Each specimen was kept at test temperature for about 20 minutes prior to testing. Optical fractography and limited electron fractography was performed on the specimens to determine fracture origins and the degree of slow crack growth.

Results and Discussion

(1). Young's Modulus, Poisson's Ratio, Density, Fracture Toughness and Microstructure

The measured Young's modulus, Poisson's ratio, density and fracture toughness of the material were found to be 286.3 ± 1.5 GPa, 0.28 ± 0.10 , 3.31 ± 0.01 g/cm³ and 6.34 ± 0.66 MPa/m, respectively, as presented in Table 1. The value of fracture toughness, $K_{IC} = 6.34$ MPa/m, is higher than that (usually $K_{IC} = 4-5$ MPa/m) observed from more conventional equiaxed, fine grained silicon nitrides. As seen in Figure 1, the material exhibits a elongated grain structure. This elongated microstructure gave rise to a relatively high fracture toughness similar to those frequently exhibited by other "in situ toughened" silicon nitrides with highly elongated grain structures [3-5]. Polished sections of the material indicated an unusually large amount of porosity as seen in Figure 2.

(2). Strength

The results of the strength testing are shown in Figure 3, where strength was plotted as a function of temperatures from 25 to 1300°C. The strengths were 715.6 ± 75.1 , 599.4 ± 40.7 , 598.0 ± 29.5 , and 566.8 ± 74.5 MPa, respectively, at RT, 1150, 1260, and 1300°C. Strength degradation relative to the room temperature value is relatively small with about 16, 16, and 24 % at 1150, 1260 and 1300°C, respectively. It is suspected that a sudden strength degradation might take place at temperatures > 1300°C.

(3). Dynamic Fatigue

For most ceramics and glasses, slow crack growth can be expressed by the empirical relation $v = AK_I^n$, where A and n are slow crack growth parameters associated with material and environment, and K_I is the Mode I SIF. For dynamic fatigue testing which employs constant loading (P) or stressing rate (σ), the corresponding fatigue strength (σ_f) is expressed [6]

$$\sigma_f = [B'\sigma]^{1/(1+n)} \quad (1)$$

where B' is a parameter associated with A, n, fracture toughness, inert strength, crack geometry and loading configurations. The slow crack growth parameters n and B' can be obtained, respectively, from the slope and intercept of the dynamic fatigue curve when fatigue strength ($\text{Log } \sigma_f$) is plotted as a function of stressing rate ($\text{Log } \sigma$). In turn, the parameter A can be obtained from B', n, inert strength, and crack and loading configurations in conjunction with an appropriate equation [6].

A summary of the dynamic fatigue results is presented in Table 2. As seen in the table, the decrease in fatigue strength with decreasing loading rate, which represents fatigue susceptibility, was not significant at temperatures of 1150 and 1260°. This can be seen more clearly in a dynamic fatigue curve shown in Figure 4, where individual fatigue strength ($\text{Log } \sigma_f$) was plotted as a function of applied stressing rate ($\text{Log } \sigma$) according to Eq. (1). At a temperature of 1260°C, the material exhibited almost no fatigue with a considerably large fatigue parameter of $n = 430$. However, at a lower temperature of 1150°C, an increase in fatigue strength with decreasing loading rate was evident, as seen in Figure 4. This increase in strength with decreasing loading rate, similar to the phenomenon known as 'the strain- or stressing- rate reverse effect,' has been frequently observed by the authors for NC 433 SiC [7], SN 260 Si₃N₄ [8], SN 252 Si₃N₄ [9], SN 251 Si₃N₄ [10], AS 700 Si₃N₄ [11] and some alumina materials [12]. It is speculated that crack-tip blunting via crack-tip deformation and/or oxidation dominated the slow crack propagation, thereby resulting in a strength increase at lower stressing rates.

The fact that SNW 1000 silicon nitride material does not exhibit any fatigue at 1150 and 1260°C is contradictory to the results recently obtained by Liu et al [13]. They reported that microwave-annealed SNW 1000 silicon nitride under pure tension exhibited an appreciable fatigue susceptibility even at 1200°C in air with a fatigue parameter of $n \approx 20$ (The authors calculated this fatigue parameter based on their published

data [13]). Some possible reasons for this inconsistency are material inhomogeneity and/or a difference in microstructures obtained via microwave- and conventional (the method used in this work)- annealing. Also, crack blunting which can be thought of as an oxidation-enhanced process was probably involved in the failure of the flexural specimens as the highest stresses are on the surface. However, blunting might not have been involved in the operative failure process of the tensile specimens because the stress is uniformly distributed throughout the test section and thus slow crack growth of internal (volume), unblunted flaws could dominate. If there is no difference in homogeneity and microstructure between the two materials, crack blunting is believed to be the major mechanism that results in a difference in fatigue behavior between the two materials. A fatigue study using flexure specimens made from the same material lot as that used for the tensile testing, (or using flexure specimens cut from the tension remnants) would verify this hypothesis.

A decrease in fatigue strength with decreasing stressing rate was observed only at a temperature of 1300°C. Therefore, extensive dynamic fatigue testing was conducted at this temperature using fifteen specimens at each loading rate with a total of three loading rates. The dynamic fatigue results obtained at this temperature are presented in Table 2. The results are also depicted as a dynamic fatigue curve in Figure 5. The slow crack growth parameter that was evaluated based on Eq. (1) with the mean (arithmetic) values was $n = 40.7$. Note that a slight increase in temperature from 1260 to 1300°C makes a great difference in fatigue behavior of this material.

The Weibull strength distributions obtained at each stressing rate are presented in Figure 6. The Weibull parameters (Weibull modulus, intercept and Weibull median strength) based on the least-square method are summarized in Table 3. The Weibull modulus was estimated to be 8.54 ± 0.82 , 10.39 ± 1.31 and 10.63 ± 0.78 , respectively, at stressing rates of 2000, 63 and 2 MPa/min. These Weibull moduli are within the range (= 8 to 15) commonly observed for most silicon nitride ceramics at elevated temperatures. The Weibull median strengths, corresponding to a failure probability of 50 %, were 574.8, 508.2 and 486.3, respectively, at 2000, 63 and 2 MPa/min.

Due to the exponential-dependence of lifetime on applied stress ($t_f = \alpha[\sigma_a]^{-n}$, where t_f and σ_a are lifetime and applied stress, respectively), the fatigue parameter n governs the overall lifetime of ceramic components for a given condition. By contrast, lifetime is only a linear function of α which contains the fatigue parameter 'A', thereby resulting in much less sensitivity of fatigue life to 'A', as compared to n . Therefore, it is very important to evaluate the fatigue parameter n as accurately as possible. Various methods and analyses have been developed in the past two decades to determine the fatigue parameters n and A . Since the strength variability of ceramic materials is significant, most methods apply Weibull statistics to characterize either inert or fatigue data. The statistical methodologies developed based on the dynamic fatigue equation Eq. (1) include: least squares of the individual data, the simple (arithmetic) mean or the Weibull median values; bivariate and trivariate methods [14]; and the statistical reproducibility technique [15,16], etc. Table 4 presents the values of fatigue parameter n determined from Weibull

median, arithmetic mean, individual data and statistical reproducibility methods. The median value, least squares and median deviation techniques are being developed by NASA Lewis for CARES/LIFE codes. Table 4 also includes the coefficient of variation in 'n' determined with each method. The results in Table 4 indicates that there is little difference in the values of n obtained from the four different methods, with n ranging from 40.3 to 41.4. This indicates that any of the methods could have been adopted to estimate a reasonably accurate fatigue parameter n from the fatigue data obtained at 1300°C.

As stated above, since the lifetime is very sensitive to the fatigue parameter n, the statistical reproducibility of n is also of a great importance. Therefore, reproducibility analysis of n was made here, based on the analysis made by Ritter et al [15]. The coefficient of variance in n, $C.V(n)$, can be expressed [15]:

$$C.V(n) \approx \frac{K_d}{\sqrt{J_o} m_i [R(\ln \dot{\sigma})]^{1/2}} \frac{(n-2)(n+1)}{n} \quad (2)$$

where

$$R(\ln \dot{\sigma}) = \frac{1}{J_2} \sum_{j=1}^{J_2} [\ln \dot{\sigma}_j - \ln \dot{\sigma}]^2$$

$$\ln \dot{\sigma} = \frac{1}{J_2} \sum_{j=1}^{J_2} \ln \dot{\sigma}_j$$

J_o = total number of test specimens used in experiment,
 J_2 = number of stressing rates,
 m_i = inert Weibull modulus, and
 $K_d \approx 1.44$ for most ceramics.

Figure 7 shows $C.V(n)$ as a function of total number of test specimens for different fatigue parameters of n. The fatigue parameters used here represent the values evaluated from the different methods listed in Table 4. The actual three stressing rates of 2000, 63 and 2 MPa/min were used. A value of $m_i \approx 10$ was assumed. Because of little difference in n values, $C.V(n)$ is insensitive to n but very sensitive to total number of test specimens particularly at $J < 50$. A summary of $C.V(n)$ obtained from the experiments are presented in Table 4. Equation (2) predicted a value of $C.V(n) = 0.252$, while the experimentally obtained $C.V(n)$ ranges from 0.275 to 0.284. This clearly indicates that the statistical reproducibility analysis agrees reasonably with experimental data (see also Figure 7). Hence, based on Eq. (2), one can conveniently predict the degree of statistical reproducibility of n as a function of the number of test specimens for a given set of stressing rates (number and range) and the

inert Weibull modulus.

The evaluation of fatigue parameter 'A' requires a value of "inert" strength (i.e. that strength for which no crack extension or weakening of the initial flaw population has occurred). In room temperature slow crack growth due to stress corrosion, inert strength of a ceramic material can be obtained routinely at any stressing rate by using an appropriate, chemically inert medium such as silicon oil or liquid nitrogen. However, the exact concept and definition of "inert" strength at elevated temperatures can be disputed in view that the inert strength represents that measured without any slow crack growth and/or that determined without the weakening environment (i.e. temperature). As temperature is the environment that weakens the glassy grain boundaries and promotes crack growth, it must be eliminated or restricted to approach the "inert" condition. Further, temperature may induce a new population of flaws (e.g. glassy regions that are strong at room temperature, but weak at elevated temperature).

If one assumes that the same flaw population dominates at room and elevated temperatures, and that no local weakening (i.e. constant toughness and elastic modulus) occurs, the room temperature and inert strengths might be equivalent. This would seem unlikely as most properties change with temperature, albeit slowly. Instead, dynamic fatigue testing with a series of very high stressing rates might be used to eliminate or minimize fatigue, so that in principle, the strength converges to one particular value. An analytical solution by the authors show that convergence should occur. The dynamic fatigue approach is time consuming and costly. Furthermore, it is questionable whether typical testing machines and transducers (e.g. load cell) are capable of such testing. Currently, an attempt to obtain high temperature "inert" strength, which is based on the convergence concept of fatigue strength at very high stressing rates, is in progress.

Fracture surfaces of the dynamic fatigue specimens tested at 1150 and 1260°C at either stressing rate (2 and 2000 MPa/min) did not reveal any appreciable signs of slow crack growth. This indicates that fast fracture from material defects was the prevailing mode of failure. Similar behavior to this was exhibited by most of the specimens tested at the fast stressing rate (2000 MPa/min) at 1300°C. In contrast, slow crack growth patterns were clearly observed on specimens tested at the low stressing rate (2 MPa/min) at 1300°C. This is consistent with the dynamic fatigue curve shown in Figure 4, in which the strength loss due to slow crack growth was significant at 1300°C. Typical fracture surfaces of the specimens tested at 1300°C at 2000 and 2 MPa/min are shown in Figure 8 as observed optically. The specimens tested at 2000 MPa/min exhibited what appeared to be small growth zones in some cases and a fast fracture mode in others. Scanning electron fractography will be necessary to determine the exact failure mode.

Conclusions

The dynamic fatigue results indicate that flexural fatigue susceptibility of SNW 1000 Si_3N_4 is negligible at test temperatures $\leq 1260^\circ\text{C}$, but becomes significant at a temperature of 1300°C with a fatigue parameter of $n = 40$. It is noteworthy that the small increase in temperature from 1260 to 1300°C gives rise to significant fatigue susceptibility of the material. The estimated fatigue parameter of $n \approx 40$ and coefficient of variation of $C.V(n) \approx 0.28$ were consistent regardless of the method of estimation.

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Status of Milestones

Milestones are on time.

Communication/Visits/Travel

Presented a paper entitled "Measurement and Modeling of Strength Distributions Associated with Grinding Damage," at the annual ACS meeting April 24-26, 1994.

Problems Encountered

Availability of *in situ* toughened Si_3N_4 's is limited.

Publications

1. "Thermal Shock Behavior of Silicon Nitride Flexure Beam Specimens with Indentation Cracks," S. R. Choi and J. A. Salem, J. Am. Ceram. Soc., 77[3] 835-38 (1994).
2. "Thermal Expansion and Elastic Anisotropy in Single Crystal Al_2O_3 and SiC Reinforcements," J. A. Salem, Z. Li and R.C. Bradt, NASA TM 106516.
3. "Crack Growth Resistance of *in Situ*-Toughened Silicon Nitride," S. R. Choi and J. A. Salem, J. Am. Ceram. Soc., 77[4] 1042-46 (1994).

Table 1. Young's modulus, Poisson's ratio, density and fracture toughness of SNW 1000 silicon nitride

Young's Modulus ¹ E (GPa)	Poisson's Ratio ² ν	Density ³ ρ (g/cm ³)	Fracture Toughness ⁴ K_{Ic} (MPa/m)
286.3 $\pm$ 1.5	0.28 $\pm$ 0.10	3.31 $\pm$ 0.01	6.34 $\pm$ 0.66

1. By the impulse excitation technique (24 flexure specimens)
2. By the impulse excitation technique (11 disk specimens)
3. By the specimen mass/volume method (12 specimens)
4. By the SEPB method (5 specimens)

Table. 2. Summary of dynamic fatigue results of SNW 1000 silicon nitride

Temperature T (°C)	No. of Specimens	Stressing Rate $\dot{\sigma}$ (MPa/min)	Mean Fatigue Strength σ_f (MPa)
1150	5	2	785.6(47.9)*
1150	5	2000	599.4(40.7)
1260	5	2	588.5(55.6)
1260	5	2000	598.0(29.5)
1300	15	2	480.1(74.5)
1300	15	63	501.5(49.5)
1300	15	2000	566.8(74.5)

Notes:

Specimen dimension: 2.86(H) x 3.66(W) x 38(L) mm³.

15/30 mm spans (four-point).

* The parenthesis indicates one standard deviation.

Table 3. Summary of Weibull parameters obtained from different stressing rates for SNW 1000 silicon nitride

Temperature (°C)	Stressing Rate (MPa/min)	Number of Specimens	Weibull Parameters		
			Weibull modulus	Intercept Ln(MPa)	Weibull Median (MPa)
1300	2000	15	8.54	-54.64	574.8
	63	15	10.39	-65.08	508.2
	2	15	10.63	-66.13	486.3

Notes:

- a. Specimen dimensions: 2.86(H) x 3.66(W) x 38(L) mm³.
- b. 15/30 mm spans (four-point).

Table 4. Summary of fatigue parameter (n) and coefficient of variation in n (C.V(n)) determined from various methods.

Method	n	C.V(n)
Weibull median	40.298 ± 11.241	0.279
Arithmetic mean	40.740 ± 11.554	0.284
Individual data	41.418 ± 11.391	0.275
Statistical reproducibility [12]	40.740 ± 10.260	0.252

Figure 1. Microstructure of SNW 1000 silicon nitride.

Figure 2. Polished surface of SNW 1000 silicon nitride showing pores.

Figure 3. Strength as a function of temperature for SNW 1000 silicon nitride. Error bar indicates one standard deviation.

Figure 4. Dynamic fatigue results of SNW 1000 silicon nitride at temperatures of 1150 and 1260°C in air.

Figure 5. Dynamic fatigue results of SNW 1000 silicon nitride at a temperature of 1300°C in air.

(a)

Figure 6. Weibull strength distributions for different stressing rates obtained at 1300°C in air for SNW 1000 silicon nitride: (a) 2000 MPa/min; (b) 63 MPa/min; (c) 2 MPa/min.

Figure 6 (continued). Weibull strength distributions for different stressing rates obtained at 1300°C in air for SNW 1000 silicon nitride: (a) 2000 MPa/min; (b) 63 MPa/min; (c) 2 MPa/min.

Figure 7. Coefficient of variation in n ($C.V(n)$) as a function of total number of test specimens with different n values, based on the reproducibility analysis [15]. The experimental data are also shown.

(a)

(b)

Figure 8. Typical fracture surfaces of specimens subjected to dynamic fatigue testing at 1300°C in air for SNW 1000 silicon nitride: (a) $\dot{\sigma} = 2000$ MPa/min, $\sigma_f = 639$ MPa; (b) $\dot{\sigma} = 2$ MPa/min, $\sigma_f = 385$ MPa.

Life Prediction Methodology

D. Wu (AlliedSignal Engines)

Objectives/Scope

AlliedSignal Engines has defined a program that builds on the progress made in Phase I of the Life Prediction Methodology for Ceramic Components of Advanced Heat Engines program. This Phase II program will develop the methodology required to adequately predict the useful life of ceramic components used in advanced heat engines. Phase II will concentrate on predictive methodology for time- and cycle-dependent failure modes, as well as proof testing and nondestructive evaluation (NDE) methodology that will enhance component reliability through screening of low-strength components.

The life prediction methodologies developed will be generic and hence will be applicable to ceramic components that operate under known temperature and stress conditions. It is anticipated that the methodologies will be particularly useful to the automotive industry for components such as turbochargers, cam followers, valves, etc.

Progress During December, 1993 Through March, 1994

Since receiving the Phase II contract go-ahead on December 1, 1993, the AlliedSignal Ceramic Life Prediction team has finalized most of the details of the Phase II effort, and has made significant progress towards the objectives of the program.

The technical effort has been organized into six objective-oriented tasks, as follows:

1. Material Baseline
2. Compressive Creep Methodology
3. Flaw Growth Methodology
4. Cyclic Fatigue Methodology
5. Proof Test Methodology
6. NDE Reliability Methodology

The program organization and the overall program plan were presented at the Phase II Kickoff Meeting held in Phoenix, Arizona on February 15, 1994. These plans and further progress are described below.

1. Material Baseline

This task includes activities for:

- a. Procurement of all NT154 silicon nitride specimens required for the Phase II program from Norton Advanced Ceramics in Worcester, Massachusetts
- b. Specimen testing to ensure that the newly-procured material is similar to that used in previous testing conducted during Phase I
- c. Specimen testing to determine the strength and life characteristics of as-processed surfaces
- d. Specimen testing to complete the information acquired during Phase I dealing with surface strength and surface condition issues:
 - Surface strength of machined spin disks
 - Surface strength of notched tensile specimens

A purchase order has been placed with Norton Advanced Ceramics (NAC) for the manufacture of the required amount of raw ceramic powder (all specimens will be procured from one master lot, to ensure consistency) and the engineering for specimen manufacture.

Based on lessons learned from Phase I of this program, a detailed sequence of design and manufacturing steps has been agreed to between NAC and AlliedSignal. For each specimen "Job", the following steps are to be followed:

1. Specimen Design Review
2. Finalize specimen quantity to be manufactured and delivered
3. Complete Job Pre-Engineering (specification of detailed routing)
4. Define fabrication and delivery schedule
5. Fabricate and deliver First Article
6. Fabricate and deliver balance of specimens for Job

7. Prepare and forward the following items for "Deliverable Package"
- All excess blanks and finished specimens
 - All rejected blanks (i.e., with "Atypical Defects")
 - All powder batch and component batch mechanical properties (including raw data and broken failure-tested bars)
 - All specimen inspection data, including fluorescent penetrant inspection (FPI) maps and microfocus x-ray (MFXR) films
 - Process Control charts
 - Other manufacturing data as requested.

The test matrix for this task is shown in Table 1-1.

2. Compressive Creep Methodology

The objective of this task is to obtain creep data under compressive loading to complement the tensile creep data and model obtained during Phase I, such that stress-relaxation and creep deformation in ceramic advanced heat engine components can be reliably predicted.

Consultations have been held with Drs. M. Ferber and A. Wereszczak of the Oak Ridge National Laboratory High-Temperature Materials Laboratory (ORNL-HTML). The test matrix established is shown in Table 2-1.

TABLE 1-1. MATERIAL BASELINE TEST MATRIX.

Specimen Type(s)	Test Temperatures, F							
	75	1300	2100	2200	2300	2400	(TBD)	2500
	No. Of Specimens							
MIL-B Flexure (Machined)*	30	10	10	--	--	--	30	10
Tensile FF (Machined)*	--	--	10	10	--	--	--	10
Tensile S/R (Machined)*	--	--	--	10	--	--	--	10
Tensile S/R (Transverse Machined)	--	--	--	10	--	--	--	10
Tensile S/R (As-Processed)	--	--	--	10	--	--	--	10
MIL-B Flexure (As-Processed)	60	--	--	--	--	--	--	--
Spin Disk Cut-Up Surface	100	--	--	--	--	--	--	--
Low and High KT	10	--	--	--	--	--	--	--
* Tests to confirm material similarity to NT154 used in Phase I.								
FF = Fast Fracture. S/R = Stress/Rupture.								

3. Flaw Growth Methodology

The objective of this task is to obtain explicit flaw growth information such that Subcritical Crack Growth (SCG) parameters obtained from indirect measurements such as stress rupture experiments can be independently validated. If explicit flaw growth information can be reliably obtained, this would be a low-cost alternative to the indirect measurements that are in use at present.

Detailed discussions have been held with Professor R. Dauskardt of Stanford University on advanced experimental techniques that can be applied to crack monitoring. The current test matrix, based on pre-flawed tensile specimens, is shown in Table 3-1. Additional (flexure) specimens may be added to the test matrix at a later date.

4. Cyclic Fatigue Methodology

The objective of this task is to develop a life prediction model for ceramic components subjected to cyclic loading. The effects of loading variables (R-ratio and hold time) as well as surface condition (as-densified, transverse machined, and longitudinal machined) will be studied. Based on the findings, correlations will be attempted with the SCG data/model developed previously during Phase I. Consultations have been held with Drs. M. Ferber and A. Wereszczak of ORNL-HTML. The test matrix is presented in Table 4-1.

TABLE 2-1. COMPRESSIVE CREEP TEST MATRIX.

Specimen Type	Test Temperatures,F		
	2300	2400	2500
	No. of Specimens		
Axial (Machined)	8	8	8

12025(02)

TABLE 3-1. FLAW GROWTH TEST MATRIX.

Specimen Type	Test Temperatures,F			
	2100	2200	2300	2400
	No. of Specimens			
Tensile (Machined)	5	5	5	5

12025(03)

TABLE 4-1. CYCLIC FATIGUE TEST MATRIX.

Specimen Type(s)	Test Temperatures,F						
	75	1300	2100	2200	2300	2400	(TBD)
	No. Of Specimens						
Tensile, R = 0 (Machined)	--	16	--	16	--	--	--
Tensile, R = 0 (Machined, 60-Sec hold)	--	8	--	8	--	--	--
Tensile, R = -1 (Machined)	--	10	--	10	--	--	10
Flexure, Tension-Tension (Longitudinal Machined)	15	15	25	25	--	--	--
Flexure, Tension-Tension (Transverse Machined)	--	25	15	--	--	--	--
Flexure, Tension-Tension (As-Processed)	--	--	15	15	--	--	--

12025(04)

5. Proof Testing Methodology

The goal of the Phase II proof testing effort is to develop the methodology to assess the effect of proof testing on the reliability of a component for surface-induced failure modes. The ideal proof test would subject the component to conditions identical to those seen in service, but this is most often extremely difficult to do economically. For example, the only way to reproduce the exact conditions a turbine blade is subjected to would be to install the blade in an engine and run the engine over a cycle simulating all possible operating conditions. But this test would only proof test the blade for fast fracture strength and would ignore other time-dependent failure modes, such as subcritical crack growth, stress rupture, oxidation, and corrosion. Therefore, proof testing methodology to evaluate the effects of proof testing on the reliability of each possible failure mode needs to be developed.

In an effort to perform component proof testing that is economical and effective, methodologies are needed to evaluate the effects of non-ideal proof testing conditions on the in-service reliability of components. The non-ideal proof test cycles require methods to address conditions such as:

- I. Proof test temperature conditions that differ from operating temperature conditions (i.e., room-temperature proof testing for high-temperature service conditions)
- II. Proof test conditions that do not adequately stress all high-risk locations (i.e., proof testing of a bend bar in three-point bending for final fracture of the specimen in four-point bending)

- III. Proof test conditions in fast fracture for time-dependent failure modes.
- IV. Proof test stress conditions that differ from operating stress conditions, such as:
- Off-Axis loading
 - Differing degrees of multiaxiality

The Phase II proof testing program has been structured so that theoretical developments are performed concurrently with the specimen testing program. The results of the testing program will be used to ascertain the applicability of the methodology developed and to readdress the efforts in case of discrepancies. The efforts will address the surface failure modes of the components. The test matrix is shown in Table 5-1.

Two types of surface conditions are typically encountered in components: as-densified and machined surfaces. The as-densified surface flaw distribution is commonly assumed to be isotropically (uniformly) distributed. In the case of machined surfaces, Rice and Mecholsky (1,2) explain that grinding produces two populations of surface flaws: one set aligned with (along) the grinding direction, and a second perpendicular to it. Data from the Phase I Ceramic Life Predication program (3) suggests that the flaws along the grinding direction can be assumed to be anisotropically distributed (i.e., flaws aligned in a preferential direction); whereas, the second set of flaws are isotropically distributed (i.e., flaws aligned randomly in all directions). These distribution functions are shown schematically in Figure 5-1.

TABLE 5-1. PROOF TESTING TEST MATRIX.

Specimen Type(s)	Test Temperatures, F		
	75	2100	2200
	No. Of Specimens		
I. Residual Strength (3-pt/4-pt)	30		
II. Residual Strength (RT/HT)	--	30	30
III. Dynamic Fatigue (Flexure)			
Proof Tested, Rate 1	9	9	9
Proof Tested, Rate 2	9	9	9
Non-Proof Tested, Rate 1	9	9	9
Non-Proof Tested, Rate 2	9	9	9
IV. Non-Proportional Loading			
Round Plate (Machined)	60*	30	--
Round Plate (As-Processed)	30	--	--
Anisotropy (MIL-B Flexure)	150	--	--
*30 Specimens will be tested off-axis; 30 specimens will be tested in plate-bending mode (biaxial stress field).

Figure 5-1. Graphical representation of the distribution functions of the flaw populations in a ground (machined) surface. (a) Functions for flaws normal to the machining direction; (b) Functions for flaws along the machining direction.

In order to clearly understand the effects of non-ideal proof testing conditions, we must begin by identifying and addressing the complications at their lowest level. The first complication deals with the type of surface that is being tested. Is the surface machined or as-processed? Has the machined surface been proof tested for flaws aligned with the machining direction or perpendicular to the machining direction? In short, is the proof testing on an isotropic surface or is it on an anisotropic surface? As a result, both types of flaw distributions are being studied in this program.

The second complication deals with a ceramic material property: the shear sensitivity. If a material is shear sensitive, failure will also occur for those cases when the combination of the resolved shear and normal stresses on the flaw exceed the strength of the material. Therefore, before proceeding to perform proof testing studies, the shear sensitivity of the material must be determined. A program to determine the shear sensitivity of the selected NT154 silicon nitride material is an integral part of this effort. Figure 5-2 shows the variation of effective stress as a function of off-axis orientation. This Figure shows that for a very shear-sensitive material, the effective stress is higher at off-axis locations (for a uniaxial stress field). This means that it is easier for cracks to fail that are not aligned (in terms of crack face vector) with the applied stress direction.

Figure 5-2. Effects of shear sensitivity, Q , on the effective stress of a unidirectional stress field at off-axis orientations.

The third set of complications includes those related to the proof testing technique, described in the list at the beginning of this section. The approach to study these complications is explained in the following sections. The planned study incorporates "lessons learned" during the Phase I program. From those efforts, it was learned that in order to obtain proof test specimens with the same surface properties as the proof test components, it is necessary to machine each specimen from the component itself. Hence, proof test components have been designed that will be easily machined into specimens which will in turn be used to generate a baseline proof test data base which includes the shear sensitivity value.

A 51 by 51 mm square tile was chosen as the baseline specimen for the proof testing portion of this program. Tiles with both as-processed and machined surface conditions will be machined into MIL-B test bars and into plate specimens for material property data generation and proof testing. The machined surface specimens will be machined at angles of zero (longitudinal), 90 (transverse), 50, 60, 65, and 70 degrees. Thirty specimens of each machining direction will be tested, for a total of 180 specimens (including 30 specimens from the material baseline test matrix). Additionally, thirty as-processed surface specimens will be tested, to determine the as-processed Weibull parameters. The longitudinally-machined specimens will provide data on the strength distribution for flaws perpendicular to the machining direction. Based on the findings from the Phase I program, these flaws are isotropically distributed. The transverse-machined specimens will provide data on the strength distribution for flaws aligned with the machining direction (an anisotropically-oriented flaw distribution).

The intermediate-angle machined specimens, together with the transverse-machined specimens will be used to determine the shear sensitivity of the material. The machined specimens should provide a better estimate of the shear sensitivity of the material, because the data is obtained from the small flaws produced by the grinding process, contrary to the shear sensitivity values obtained through diametral compression or notched tension-torsion specimens, which exhibit relatively large cracks.

Two types of specimens will be machined from the tiles for proof testing: MIL-B bend bars and plate specimens. A group of transversely-machined bend bars will be tested to determine the residual strength of the bars at elevated temperature after proof testing at room temperature. The bend bars will be proof tested in a four-point bend format to a stress level predetermined from the baseline data base, with the goal of breaking 30 percent of the specimens. Following proof testing at room temperature, the specimens will be loaded to failure at elevated temperature, in four-point bending. These tests will show the effects of proof testing at room temperature for high-temperature service conditions.

A second group of bars will be proof tested in three-point format, with the goal of breaking 30 percent of the specimens, and the remaining bend bars will be tested to failure in a four-point format. These tests will show the effects of component proof tests that do not adequately proof all the highly-stressed locations. A third set of transversely-machined specimens will be proof tested at room temperature and later tested to failure under a dynamic fatigue test. These specimens will provide information on the effects of proof testing on the time-dependent failure modes.

Off-axis loading and multiaxial tests will be performed on plate specimens. These plates will be proof tested under a three- or four-point bend format, depending on which is determined to be more effective later in the program. For the off-axis loading, these plates will be rotated X number of degrees relative to the proof testing orientation and then tested to failure. The degree of rotation will depend upon the shear sensitivity value for the material. The multiaxial effect plates will be tested under a plate bending format.

The above paragraphs describe the proof testing effects and approaches for the machined specimens, with an assumed anisotropic flaw distribution. The effects of proof testing on the isotropic flaw distribution will be investigated using as-processed surface specimens. The effects of proof testing with off-axis loading and inadequately stressining of high-risk locations are the only effects that will be studied for the as-processed surface specimens. The assumption is made that the methods derived for the machined surfaces will carry over to the as-processed surfaces.

6. NDE Reliability

The objective of this task is quantify the probability of detection (POD) of surface flaws in ceramics for various nondestructive evaluation (NDE) techniques, such that NDE can be fully integrated into life prediction methodology for ceramic components. The objective will be accomplished through a comprehensive reliability study.

Discussions have been held with Dr. A. Berens at the University of Dayton Research Institute (UDRI) regarding the design of the reliability study. Placement of a formal purchase order at UDRI is now in progress. UDRI will provide consultation regarding the reliability study design, as well as statistical analysis tools for determining POD.

The proposed test matrix for this task is shown in Table 6-1.

TABLE 6-1. NDE POD TEST MATRIX.

Specimen Type	No. Of Specimens
Square Plate > Bar (Machined)	4
Square Plate > Bar (As-Processed)	4
GTCP85 APU Stators (Machined)	55
GTCP85 APU Stators (As-Processed)	55

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3.3 ENVIRONMENTAL EFFECTS

Environmental Effects in Toughened Ceramics*

G. A. Graves, Jr. (University of Dayton)

Objective/scope

Since December 1984, the University of Dayton has been involved in a five-phase project to investigate the effects of environment on the mechanical behavior of commercially available ceramics being considered for heat engine applications. In the first phase of this project, the effects of environment on the mechanical behavior of transformation-toughened ZrO_2 ceramics were investigated. In the second phase, two Si_3N_4 ceramics (GTE PY6 and Norton/TRW XL144) and one SiC ceramic (Hexoloy SA) were evaluated. In the third phase, the tensile, flexural, and fatigue strength of three SiC and six Si_3N_4 ceramics were evaluated at temperatures ranging from 20 to 1400°C. Microstructure, chemistry, and physical properties were also investigated. In the fourth phase, the flexural strength and fatigue behavior of two additional Si_3N_4 ceramics (Kyocera SN-260 and Garrett GN-10) were investigated. In addition, the fatigue behavior of one Si_3N_4 ceramic (Norton/TRW NT-154) was investigated. In phase five, five newly developed SiC and three newly developed Si_3N_4 ceramics are being investigated. In addition, the effects of different machining processes on the mechanical behavior of selected SiC/ Si_3N_4 ceramics will be studied.

During the past six months the project, a study to investigate the effects of various machining treatments on the flexural strength of Morton International (MI) SiC was initiated. In addition, the evaluation of an Allied Signal, Ceramic Components Division, material was initiated.

Technical progress

A machining effects study using chemical vapor deposited (CVD) beta (β) silicon carbide (SiC) was completed. Chand Kare Technical Ceramics agreed to machine SiC using various types of commercial grinding wheels and removal rates as shown in Table 1. The SiC material selected for the study was Morton International's β -SiC prepared by CVD. The material was chosen because of Chand Kare's experience with machining it and Morton International's ability to consistently prepare pore-free, high-purity, homogeneous, fine-grained material in sizes up to 1.5 m dia. x 2.5 cm thick.

In addition, UDRI has a large database on this material that was obtained through Air Force development programs, and it was felt that the material's microstructural consistency would make it a good baseline material for a machining study.

Seventy-five specimens were prepared for the study. Fifteen specimens were machined using the six types of grinding wheels and the removal rates shown in

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Table 1. The flexural strength results for each group of 15 specimens (10 fast fracture and five slow fracture) are also given in Table 1. A graphic representation of the strength results is shown in Figure 1.

Table 1. Flexural Strength Machining Effects Study (Baseline Material - CVD SiC)

Test Group	Grinding Wheel Type	Removal Rate ¹ per Pass	Total Amount Removed/Side	Average Flexural Strength	Test Conditions		No.
		mm (in)	mm (in)	MPa, Std. Dev. (Ksi, St. Dev.)	Crosshead Speed mm/s (in/min)	Temp. (°C)	Specimens Tested
22	Norton SD 150 R75B99E-1/4	0.005 (0.0002)	0.025 (0.001)	352, 29 (51, 4.3)	0.04 (0.1)	20	10
				340, 23 (49, 3.3)	0.0004 (0.001)	20	5
23	Norton SD 320 R75B99E-1/4	0.005 (0.0002)	0.20 (0.008)	383, 23 (56, 3.4)	0.04 (0.1)	20	10
				369, 15 (54, 2.1)	0.0004 (0.001)	20	5
24	General Dia. CGD600 R75B-1/4	0.0025 (0.0001)	0.025 (0.001)	454, 17 (66, 2.5)	0.04 (0.1)	20	10
				422, 52 (61, 7.6)	0.0004 (0.001)	20	5
25	Norton SD 800 R50-1/32	0.0025 (0.0001)	0.025 (0.001)	389, 32 (56, 4.6)	0.04 (0.1)	20	10
				432, 24 (63, 3.4)	0.0004 (0.001)	20	5
26	Norton SD 800 R75B56-1/4	0.0025 (0.0001)	0.025 (0.001)	478, 52 (69, 7.6)	0.04 (0.1)	20	10
				438, 91 (64, 13.2)	0.0004 (0.001)	20	5
27	Norton D 3/6 mic R75B-1/4	0.0025 (0.0001)	0.025 (0.001)	297, 65 (43, 9.5)	0.04 (0.1)	20	10
				337, 48 (48.9, 6.9)	0.0004 (0.001)	20	5

¹All specimens were ground in the longitudinal direction.

Figure 1. Flexural Strength Machining Effects Study.

In an Air Force sponsored program on CVD SiC recently concluded at UDRI (reference 1 SiC final report), it was observed by Raman spectroscopy as-received material had very low residual stresses throughout the 20 mm thick, 0.5 m diameter piece of material studied; however, there was a measurable increase in the surface strain after various finishing processes. The magnitude of the strain was dependent on the type of finishing process used. The lowest strain was observed after the material was cut with a diamond cut-off blade; strain increased significantly after diamond wheel grinding, and peaked after a series of free-diamond grit polishes.

Based on these preliminary results, a more comprehensive Raman spectroscopy study was initiated on specimens from the machining study being carried out on CVD SiC by ChandKare and UDRI. Pieces of fractured flexure specimens were selected from each of the six different groups of machined specimens for small spot Raman spectroscopy analysis. Each specimen has been examined by scanning across the surface placed in tension during the four-point bend test and down the sides of the specimen.

Four plots of data were taken on the CVD SiC specimens identified as SMG-93-2-gg-nn. The gg specification identifies the group and the nn value gives the specimen number in that group. The specimens were from groups 22, 23, 24, 26, and 27, with two specimens from each group.

The recordings of the Raman spectra of the transverse optical mode (TO) Raman line at 795 cm^{-1} were made with a Nd:YAG laser at 532 nm, a double spectrometer, and a liquid-nitrogen-cooled CCD array detector. The laser probe spot size on the specimen was a line $\sim 2\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$. Considerable care was taken to prevent any laser-induced damage to the specimen during the measurements. Examples of the spectra are shown in Figures 2 through 4. The measurement time for a typical spectrum was 10 minutes. The data has a high signal-to-noise ratio that allows very precise measurements of the full width at half maximum (FWHM), typically about 1%. This made it possible to detect very small changes in the width of the line due to the local residual surface stress. This is clearly illustrated by the two plots for specimens 26-2 (Figure 2) and 23-9 (Figure 3). Basically, the residual surface stress results from mechanical working of the material due to machining or polishing. These processes typically distort the crystalline lattice in the surface grains (i.e., introduce local strain) which effectively lowers the Q-factor of the lattice vibrations. This loss was recorded as broadening of the line, namely, as an increase in the FWHM. Theoretically, the shape of a Raman line for a good single crystalline specimen follows the Lorentzian function that is characterized by a sharp peak and slowly-decaying wings.

A good example of a minimally-disturbed line is the spectrum shown for specimen 26-2 (Figure 2). These data were taken on the end of the specimen that was only cut by a diamond saw. The fit to the Lorentzian function is quite good with an uncertainty of $<1\%$ for the resulting FWHM value. In the data analyses, the amplitude, position, background, and FWHM were fit using a nonlinear regression procedure. The effect of machining on the width is illustrated by the spectrum for specimen 23-9 (Figure 3).

Figure 2. Raman Transverse-Optical Line of CVD SiC, Specimen SMG-93-2-26-2, on the Diamond Cut, Unpolished End.

Figure 3. Raman Transverse-Optical Line of CVD SiC, Specimen SMG-93-2-23-9, on the Tension Side.

Figure 4. Raman Transverse-Optical Line of CVD SiC, Specimen SMG-93-2-27-9, Splitting Due to Bulk Stress Near One Side of the Specimen.

This specimen was submitted to 40 passes of the grinding wheel producing a considerable broadening of the line. Notice also that the fit is degraded. The observed spectra are essentially sums of contributions from the volumes of individual grains summed over several grains. These contributions would be expected to be essentially random, that is, normally distributed. When the disturbance is large, the line shape would then tend toward the Gaussian functional form with a blunt peak and faster-decaying wings. The spectrum for specimen 23-9 shows this postulated behavior.

Besides sensitivity to residual surface stress, the Raman spectrum of SiC can also reveal the presence of bulk stress. Because of the high symmetry of the lattice (cubic), the TO line is two-fold degenerate; that is, it is made up of two lattice vibrations that have the same vibration frequency in the pure single crystal form of the material. If the lattice symmetry of the grains in a local area of the specimen were strongly distorted during growth of the material, this would lower the lattice symmetry in that region. This could cause the TO line to split since the two-fold degeneracy can be supported only in lattices of high symmetry. The degree of splitting is some measure of the bulk stress; this splitting was observed in some earlier specimens of cubic CVD SiC possibly due to layering during growth. In the 10 specimens of this study, splitting was observed on one edge of one end of every specimen. An example of this splitting is the spectrum for specimen 27-9 (Figure 4). Some studies of this splitting were made as a function of position to better characterize these data; however, we do not know the positions of the specimens in the original slab of material were not known. More

information about the fabrication history of the specimens is required to interpret the results of these studies.

The most revealing results of these studies are presented in the bar graph (Figure 5) on which the mean values of the Raman line FWHM taken over all 10 specimens are plotted. Each specimen was scanned at 10 positions in a line spaced at five micron intervals on the tension side at approximately the same relative location. there were two specimens for each group. The 20 values of FWHM from these scans for each group were averaged and a standard deviation calculated. These mean values for the five groups are plotted as a bar graph with the standard deviation values included as error bars. The bars are plotted from left to right in the order of increasing fineness of the grinding wheel grit. Except for group 23, the mean values of FWHM fall as the grit size decreases as would be anticipated from the discussion in the second paragraph above. Group 23 is a special case because of the much larger number of passes used on these specimens. The 40 passes of the grinding wheel compared to the five and 10 passes used on the other groups clearly produced large residual stress in the specimen of this group.

To ensure that the differences in residual stress from the various groups was not due, at least in part, to variations in microstructure, a study microstructural examination was made of each group. the microstructure of the surface of the side placed in tension of a specimen from each group was examined. They were virtually identical. A typical microstructure is shown in Figure 6.

Figure 5. Relative Residual Surface Stress Due to Finish Grinding of CVD SiC.

Figure 6. CVD SiC as plasma etched.

Allied Signal Ceramic Components supplied UDRI with 15 GN-10 silicon nitride (Si_3N_4) tensile specimens for testing at three temperatures. Nine specimens were tested at room temperature (21°C), three were tested at 1204°C , and three at 1371°C . A summary of the results of the tensile tests are shown in Table 2.

Table 2. Fast Fracture Tensile Strength of GN-10 Silicon Nitride

Specimen Number	Test Temp. ($^\circ\text{F}/^\circ\text{C}$)	Tensile Strength		Fracture Origin
		(ksi)	(MPa)	
SMG-94-1-12-1	70 / 21	98.0	676	Vol. @ Incl.
SMG-94-1-12-2	70 / 21	100.0	689	Vol. @ Incl.
SMG-94-1-12-3	70 / 21	97.9	675	Vol. @ Incl.
SMG-94-1-12-4	70 / 21	81.6	563	Surface
SMG-94-1-12-5	70 / 21	70.3	485	Vol. @ Incl.
SMG-94-1-12-6	70 / 21	102.3	706	Vol. @ Incl.
SMG-94-1-12-7	70 / 21	94.8	654	Vol. @ Incl.
SMG-94-1-12-8	70 / 21	105.8	730	Volume
SMG-94-1-12-9	70 / 21	95.7	660	Vol. @ Incl.
	Average (St. dev.)	94.1 (11.2)	648 (77)	-
SMG-94-1-13-1	2200 / 1204	90.4	624	Surf. @ Incl.
SMG-94-1-13-2	2200 / 1204	70.6	487	Vol. @ Incl.
SMG-94-1-13-3	2200 / 1204	96.3	664	Vol. @ Incl.
	Average (St. dev.)	85.8 (13.5)	591 (93)	-
SMG-94-1-16-1	2500 / 1371	59.3	409	Surface
SMG-94-1-16-2	2500 / 1371	40.6	280	Surface
SMG-94-1-16-3	2500 / 1371	56.4	389	Surface
	Average (St. dev.)	52.1 (10.1)	359 (69)	-

Most of the specimens failed at volume inclusions associated with iron inclusions. One atypical volume initiation site is shown in Figure 7 (specimen SMG-94-1-12-5).

Figure 7. Allied Signal GN-10 Atypical Fracture Initiation Site.

No other testing was accomplished due to the lack of specimens. UDRI has taken advantage of the lull in mechanical testing to repair test machines and furnaces, and to upgrade the 1361 Instron control system to the new Instron computer. The test machines and load cells have also been recalibrated.

Numerous discussions have been held with the four companies who have expressed interest in supplying specimens to UDRI for mechanical property characterization and the planned finishing study.

Dow Chemical, Allied Signal (Ceramic Components Division), Carborundum, and Kyocera have furnished lists of type of material and the quantity they will supply, tests they desire to have run, and delivery dates.

Tables 3 through 7 were organized by task to reflect the original test matrix proposed to ORNL, and the number of specimens in each category promised by the participating organizations.

The number of specimens indicated in the proposal is noted in regular type in the row suggesting the test conditions for the materials under investigation. For example, in Table 3, under Piston Engine Components Material A), it was suggested that 10 flexure bars be tested at room temperature at a stress rate of 4×10^{-3} m/min and 5 at 4×10^{-5} m/min, 10 were to be tested at 750°C and 4×10^{-3} m/min and 5 at 4×10^{-5} m/min, etc.

Table 3. Flexural Strength Measurements and Stress Rupture

Candidate Ceramics	Flexural Strength Measurements										Stress Rupture			
	20°C		750°C		1000°C		1250°C		1350°C		1000°C		1350°C	
	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	1/2sf	2/3sf	1/2sf	2/3sf
Piston Engine Components														
Material A)	10	5	10	5	10	5					5	5		
Dow Corning SiC			10	5	10	5					5	5		
Material B)	10	5	10	5	10	5					5	5		
Turbine engine components														
A) APUs							10	5	10	5				
Carborundum (Hexoloy SA-X)	30						20	10	20	10				
B) Automotive Turbines	10	5											5	5
C) Automotive Turbines	10	5					10	5	10	5			5	5
Kyocera, SN 253, Si3N4													5	5

Table 4. Tensile Strength Measurements

Candidate Ceramics	Tensile Strength Measurements															
	20°C		750°C		1000°C		1100°C		1200°C		1250°C		1300°C		1350°C	
	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5	4x10-3	4x10-5
Piston Engine Components																
Material A)	10	5	10	5	10	5										
Dow Corning SiC	10	5	10	5	10	5										
Material B)	10	5	10	5	10	5										
Allied Signal (AS800)	30		10		10		10		10		10		10		10	
Turbine engine components																
A) APUs	10	5	10	5	30	10	10	5	10	5	10	5	10	5	10	5
Carborundum (Hexoloy SA-X)	15				15				10	5					10	5
B) Automotive Turbines	10	5									10	5			10	5
C) Automotive Turbines	10	5									10	5			10	5
Kyocera, SN 253, Si3N4	5	5									5	5				

Table 5 . Stress Rupture and Cyclic Fatigue

<i>Candidate Ceramics</i>	<i>Stress Rupture</i>					<i>Cyclic Fatigue</i>	
	<i>1000°C</i>	<i>1100°C</i>	<i>1200°C</i>	<i>1300°C</i>	<i>1350°C</i>	<i>1000°C</i>	<i>1300°C</i>
Piston Engine Components							
Material A)	10					10	
Dow Corning SiC	10					10	
Material B)		10	10	10	10		
Allied Signal (AS800)		10	10	10	10		
Turbine engine components							
A) APUs		10	10	10			
Carborundum (Hexoloy SA-X)			10	10	10		5
B) Automotive Turbines					10		5
C) Automotive Turbines					10		5
Kyocera, SN 253, Si3N4					5		5

Table 6 . Physical Properties

<i>Candidate Ceramics</i>	<i>E</i>	<i>α</i>	<i>H/ρ</i>	<i>K_{Ic}</i>		
	<i>20-1350°C</i>	<i>20-1350°C</i>	<i>20°C</i>	<i>20°C</i>	<i>1000°C</i>	<i>1300°C</i>
Piston Engine Components						
Material A)	3	3	3	5	5	
Dow Corning SiC	3	3	3	3	5	
Material B)	3	3	3	5	5	
Turbine engine components						
A) APUs	3	3	3	5	5	5
B) Automotive Turbines	3	3	3	5	5	5
C) Automotive Turbines	3	3	3	5	5	5
Kyocera, SN 253, Si3N4					5	5

Table 7. Status of Specimens Promised and Recieved

Supplier	Contact	Phone #	Material	Flexure bars	Recieved	Date	Tensile blanks	Recieved	Date	Machined MOR	Received	Date
Allied Signal	Jim Wimmer	310-512-3183	AS800				140					
Kyocera	Dave Carruthers	206-696-8950	SN-253	20			40			165		
Carborundum	G.V. Srinivasan	716-278-3907	Hexoloy SA-X	125			60					
Dow Corning	Larry McCoy	517-496-6059	Exp SIC	77			45			40		
Totals				222	0		285	0		205	0	

The organizations participating in the study, and the numbers in the same row, noted in bold type, indicate the number of specimens promised for those test conditions by the organization. For example, Table 3 shows that Dow Corning has agreed to provide 10 flexure bars of their experimental SiC for tests done at 750°C at the stress rate of 4×10^{-3} m/min, 5 at 4×10^{-5} m/min, 10 at 1000°C and 4×10^{-3} m/min, and 5 at 4×10^{-5} m/min, etc.

Status of Milestones

Milestone 331415 has been completed. Milestones 331416 and 331417 are in progress.

3.4 FRACTURE MECHANICS

Testing and Evaluation of Advanced Ceramics at High Temperature

J. Sankar, A. D. Kelkar, and J. Neogi (North Carolina A&T State University)

Objective/Scope

The objective of this research is to test and evaluate the long-term mechanical reliability of a Si_3N_4 at temperatures upto 1300°C . The emphasis of this effort in the current year is to microstructurally characterize the specimens tested in fatigue/creep/tension, using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectral analysis (EDS).

Technical Highlights

During this reporting period microstructural characterization of mechanically tested GTE SNW-1000 materials were conducted to investigate the effect of precycling on creep and residual tensile strength.

Experimental Procedure

Transmission electron microscopy (TEM) was performed on both the untested and precycled (coaxed) specimens. Samples were prepared using standard techniques, including grinding, dimpling and ion-milling to perforation. High resolution electron microscopy (HREM) images were taken utilizing a TOPCON EM002B transmission electron microscope operating at 200-kV. Analytical electron microscopy was performed using a 200-kV TOPCON EM002A instrument equipped with an ultra-thin-window energy dispersive X-ray spectrometer (EDS).

Grain-boundary film thicknesses of as-received and tested samples were also measured by statistical analysis using HREM. The statistical measurements were performed by printing HREM images over the entire length (up to $1\ \mu\text{m}$) of a given grain boundary between two triple pockets. Every 2 cm of the enlarged prints, corresponding to about 20 nm of the interface length, a thickness data point was evaluated, giving 40 to 50 data points for each boundary. The film width was determined by using the $6.58\ \text{\AA}$ spacings of the $\{1010\}$ $\beta\text{-Si}_3\text{N}_4$ planes in the images as an internal standard [1]. The standard deviation σ was determined from the measurements using the following equation:

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

where x_i is the i th thickness measurement, $\bar{x}$ is the mean thickness value, and n is the number of film-thickness measurements.

Test Results and Discussion

The microstructure of an as-received and a fatigue tested (coaxed 50/60/70% of fatigue strength σ_f , at 1200°C, followed by tension test) sample of GTE SNW-1000 is given below:

(A) General Morphology: The microstructure of the sintered Si_3N_4 material (as-received GTE SNW-1000) generally consisted of equiaxed and acicular $\beta\text{-Si}_3\text{N}_4$ grains surrounded by an intergranular amorphous phase, a crystalline phase or a combination of both, as shown in Fig. 1. The $\beta\text{-Si}_3\text{N}_4$ grains are seen in light contrast, while the grain boundary phase appears in a darker contrast due to the much greater electron absorption of the yttrium which is concentrated in this phase as can be seen in the EDS spectra shown in Fig. 1. The acicular grains were usually 1-5 μm long with widths of $\leq 1 \mu\text{m}$. The equiaxed grains range from submicron to 1-3 μm . A small fraction of abnormal grain growth with grains several micrometers in size were also occasionally observed.

(B) Grain-Boundary Phase Crystallization: Si_3N_4 -based polyphase ceramics densified via liquid-phase sintering has been reported [8] to contain amorphous phases at triple grain junctions and grain boundaries which may be described as metal-Al-Si-O-N oxynitride glasses depending on the sintering additive composition. The as-received GTE SNW-1000 sample exhibited an amorphous intergranular phase (Fig. 2). On the other hand the TEM analysis of the tested sample revealed nearly complete crystallization of the amorphous phases at triple grain junctions (Fig. 3). Fig. 4 depicts a bright field image of the tested sample showing a large crystalline region at a multi-grain junction. The crystalline region appears to be twinned. This may have occurred due to differences in bulk modulus of the crystalline region and the surrounding Si_3N_4 grains during mechanical deformation. It has been reported [2-7] that heat treatment has so far succeeded in partial crystallization of the amorphous phases leading to improvement of high-temperature strength. Thus it can be construed that stress assisted heat treatment increased the amount of crystallization which may have caused the Si_3N_4 material (GTE SNW-1000) to retain 100% of its room temperature strength in a short time. The room temperature tensile strength of SNW-1000 is 492 MPa and it drops down to 230 MPa at 1200°C [9]. The principal devitrification products of the tested GTE SNW-1000 are $\delta\text{-Y}_2\text{Si}_2\text{O}_7$ and minor N-apatite $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ [8]. It seems that in addition to temperature, the applied fatigue stress helped aid the crystallization process of the amorphous phase.

(C) Grain-Boundary Film Thickness Measurement: Fig. 5 shows a bright field micrograph of a grain boundary between two triple junctions. Enlargements of the grain boundary as indicated by the boxed areas were used for measuring film thickness. If

Figure 1. Representative view of the microstructure of the Si_3N_4 material GTE SNW-1000 showing variable size and morphology of $\beta\text{-Si}_3\text{N}_4$ grains

Figure 2. HREM micrograph of an as-received sample of the Si_3N_4 material (GTE SNW-1000) showing amorphous phases at a triple grain junction

Figure 3. HREM micrograph of a tested sample of the Si_3N_4 material (GTE SNW-1000) showing nearly complete crystallization at a triple grain junction,

Figure 4. Bright field image of a tested sample of the Si_3N_4 material (GTE SNW-1000) showing a large crystalline region at a multi-grain junction.

an equilibrium thickness of the grain-boundary films is assumed for a given material composition, a Gaussian distribution of the data points around a median thickness value is expected. Fig. 6 depicts one small region of an amorphous grain boundary film of the as-received sample of GTE SNW-1000. For the statistical measurements, HREM images of the entire length of the interface were printed as four micrographs (as indicated in Fig. 5) and the intergranular film-thickness data determined from ~ 50 locations, as described earlier. Histograms for two different grain boundaries and, in addition, the standard deviations are also shown in Fig. 6. The two interfaces investigated statistically, yielded average film-thickness values of 11.3 and 12.7 Å. The standard deviations for both statistical measurements were 0.66 and 0.73 respectively. Thus the average film thickness of an as-received sample was 12 ± 1 Å. Fig. 7 depicts one small region of an amorphous grain boundary film of the tested sample of GTE SNW-1000. Statistical analysis of two different interfaces yielded mean film-thickness values of 12.2 and 13.3 Å with standard deviations of 0.49 and 0.76 respectively. The average film thickness of the tested sample was 13 ± 1 Å. Thus from Fig. 3 and Fig. 7, it can be concluded that devitrification is primarily restricted to multi-grain junctions and brings about an associated change in the residual glass composition. It was observed that the tested specimens revealed a slightly wider boundary than the as-received specimen (13 versus 12 Å). It has been reported [1] that even small changes in grain-boundary thickness can unequivocally be correlated to changes in grain-boundary film chemistry. EDS work done at the grain boundary revealed a higher concentration of Al and this probably played a role in increasing grain boundary thickness.

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Figure 5. Bright field micrograph of a grain boundary between two triple junctions; enlargements of the grain boundaries as indicated by the boxed areas were used for measuring film thickness.

Figure 6. HREM micrograph of an amorphous grain-boundary film in an as-received GTE SNW-1000 sample. Statistical analysis of two different grain boundaries gave mean values of 11.3 Å and 12.7 Å.

Figure 7. HREM micrograph of an amorphous grain-boundary film in a tested GTE SNW-1000 sample. Statistical analysis of two different grain boundaries gave mean values of 13.3 Å and 12.2 Å.

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Status of Milestones

On schedule

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None

Publications and Presentations

* J. Sankar, J. Neogi, S. Neogi, M. T. Dixie and R. Vaidyanathan, "Thermal and Loading Effects on Mechanical Properties of a Hot Isostatically Pressed Si_3N_4 ," to be published in ASME Transactions.

* J. Neogi, S. Neogi, J. Sankar and R. Vaidyanathan, "High-Resolution Electron Microscopy of Precycled Samples of a Sintered Silicon Nitride," paper presented at the 18th Annual Conference on Composites, Materials and Structures, Jan 12-14, 1994).

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Standard Tensile Test Development

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Table I: Symbols used in this analysis, along with typical values. See Figures 1 and 2 for graphical definitions.

Symbo l	Typical value	Definition
l_g	10 mm	Gauge length of specimen
l_o	6 mm	Offset of laser from specimen center line
w_x	2 mm	"in-plane" sample width
w_z	2.5 mm	"out-of-plane" sample width
w_{fy}	2 mm	flag width as seen by laser
w_{fz}	2 mm	depth of flag perpendicular to scan direction
ρ		specimen bending radius
ϕ_u	10°	upper flag attachment angle
ϕ_l	10°	lower flag attachment angle
Ψ_u	0°	upper flag revolution angle
Ψ_l	0°	lower flag revolution angle
w_{fs}	2.6 mm	flag attachment slot width
w_{fa}	1 mm	width of flag at attachment point

Introduction

Laser extensometry is a convenient method for measuring strain during high temperature creep tests [1]. This report investigates the errors and uncertainties associated with this technique, and their relative contributions to the strain measurement error. Others have studied the effects of specimen bending during tensile testing, the pertinent references are listed [1-8], but no one, as far as we are aware, has examined the nature of strain measurement errors germane to laser extensometry.

In laser extensometry as implemented in our and other laboratories, the gauge length is marked by SiC flags, which hang off the specimen, supported by the friction induced by their own weight. These flags interrupt a scanned laser beam which is projected through the furnace. On the opposite side of the furnace from the laser scanner, the scan impinges on a photocell. From the time varying output of the photocell, the main processor of the laser extensometer can calculate the distance between the flags. Errors in the gauge length measurement will arise due to specimen bending, flag rotation and/or slippage and non-parallelism of the flags. Each of these is addressed in turn with specific examples.

There are two types of error which can arise during strain measurement by laser extensometry. The first, which we denote as bending/motion error, occurs because of bending or translation of the specimen, or motion of the flags themselves. These errors typically have an additive or multiplicative effect on the measurement of the gauge length. Unlike the first type, the second, which we denote as uncertainty error, results in uncertainties in the magnitude of the gauge length itself. In this section we will detail our calculations of both types of error, concentrating on the former type. In a later section we will demonstrate the effect that some of these errors might have by creating simulated creep curves convolved with the strain measurement errors.

Figure 1: Sample geometry used.

Some background in our strain-measurement technique is necessary to understand the plots that follow. Figure 1 is a schematic of the orientation of the flags and the specimen. Typically, the flags are oriented so that they project outward normally from the specimen in the plane defined by the head of the specimen. In addition, we have found it useful, and this note will demonstrate some of this utility, to make additional length measurements during the creep test. Typically, we

measure the distance between the tops of the flags, l_{tt} , the distance between the bottoms of the flags, l_{bb} , and the distance from the bottom of the bottom flag to the top of the top flag. With these three measurements we can also calculate the intercepted width of each individual flag. Each of these individual measurements is available from commercial laser measurement systems. In an ideal experiment, the two gauge length measurements (l_{tt} and l_{bb}) would be equal, and the intercepted width of the individual flags would not change during the test. In real experiments, this is rarely the case.

Bending/Motion Errors

For simplicity, we will illustrate the types of errors arising from bending of the specimen by assuming that the specimen bends to a constant radius of curvature, as might happen if a pure bending moment were applied to the gauge length. This is the sort of bending that might occur, for example, if the loading holes were symmetrically displaced from the centerline of the gauge length. Other types of bending produce more complex deformations of the gauge length, which we will not consider. Assuming pure bending of the specimen simplifies the calculation of the flag positions after deformation as well. In this section we will not apply any extension of the specimen. Rather, we will examine the apparent deformations induced by pure bending of the gauge length.

Figure 1 shows the geometry of the measurement system, while Table I shows the relevant specimen geometry variables. Before considering the changes in apparent gauge length with bending, it is useful to develop a general equation which maps the position of a point on the neutral axis of the specimen from the undeformed to the deformed state. Figure 2 shows the bending of the originally straight gauge length to a radius of curvature ρ . We locate the origin of our coordinate system at the geometric center of the specimen. A point on the neutral axis (x_1, y_1) moves to a point (x_2, y_2) via the following relations:

$$\begin{aligned}x_2 &= \rho (1 - \cos(y_1/\rho)) \\y_2 &= \rho \sin(y_1/\rho)\end{aligned}$$

The coordinates in which we will have the most interest, however, are those on the flag, since it is the flag that intercepts the laser scan to produce the gauge length measurement. Because of the special choice of pure bending, any point on the flag experiences a rotation by an angle θ (see figure 2), as well as the translation. By defining a coordinate system for the flag whose origin is at (x_1, y_1) , it becomes simple to track the motion of the edges of the flag during bending of the specimen. For simple rotation of a normal coordinate system, a point (x_f, y_f) transforms to (x_f', y_f') via the relation:

$$\begin{aligned}x_f' &= x_f \cos(\theta - \phi) + y_f \sin(\theta - \phi) \\y_f' &= -x_f \sin(\theta - \phi) + y_f \cos(\theta - \phi)\end{aligned}$$

In this equation the angle θ corresponds to that shown in the figure, while ϕ represents the angle the flag makes with the specimen. For a flag projecting normal to the specimen axis, $\phi = 0$. Note that this transformation is opposite in sign from that usually defined in solid mechanics texts in that clockwise rotations are considered positive, rather than negative, to correspond with the figure.

For the case in which the specimen deforms by bending out of the plane of the flange (the so-called "out-of-plane bending") the flags will act as the arms of a pantograph. In the geometry we consider, the distance from the geometric center of the specimen to the laser scan remains constant. Because of the bending, the apparent gauge length will either increase or decrease as the laser intercepts a different part of each flag. Consider the case diagrammed in the Figure 2, where the specimen bends away from the laser scan line, and the apparent gauge length increases. The position of any point on the flag, (x_f, y_f) , in the deformed state is:

$$\begin{aligned} x_f'' &= x_2 + x_f' = x_2 \\ &+ x_f \cos(\theta - \phi) + y_f \sin(\theta - \phi) \\ y_f'' &= y_2 + y_f' = y_2 - x_f \sin(\theta - \phi) + y_f \cos(\theta - \phi) \end{aligned}$$

Figure 2: The geometry of the bending of the neutral axis of the specimen.

To calculate the apparent gauge length, we are interested in knowing the intersection of the flags with the laser scan line, positioned a distance l_0 from the centerline of the specimen. We do not know initially the coordinates of the point on the flag in the undeformed state at the intersection with the laser scan (i.e. x_f). We do know the x coordinate of the intersection of the flag with the scan in the deformed state, (i.e. $x_f'' = l_0$, in this geometry $l_0 < 0$). Solving for x_f and substituting into the equation for y_f'' yields an expression for the y coordinate of the intersection of the flag with the laser scan. Now the apparent gauge lengths with bending may be calculated.

Figure 3 shows the apparent gauge length of the specimen as a function of radius of curvature (assuming a true gauge length of 10 mm, typical for our experiments). To put the radius of curvature into proper perspective, for our 2 mm x 2.5 mm specimen, a 1000 mm radius of curvature corresponds to 10 μ m of rise displacement. That is, when the specimen is deformed to $\rho = 1000$ mm, $x_2 = 0.01$ mm. Figure 3a shows the apparent gauge length and apparent strain for several values of the

Figure 3: Apparent specimen gauge length during out-of-plane bending of the specimen.

laser scan offset, l_0 . Clearly, the mis-measurement of the gauge length increases with increasing offset. Although the absolute error is small relative to the gauge length, the typical strain-to-failure for creep-resistant silicon nitride is also only on the order of 0.01, corresponding to an extension of only 100 μm . Figure 3b shows that the mis-measurement of the gauge length is not particularly affected by the angle at which the flag hangs from the specimen, provided that the flags hang at identical angles, a point to which we will return later. Figure 3c shows that the inter-flag¹ spacing tracks the true gauge length, but is, of course, an erroneous measure of the gauge length. Finally, Figure 3d shows that the intercepted width of the flag is totally insensitive to the bending of the specimen, making it useless as a diagnostic for out-of-plane bending. Although the figure does not show this, changes in flag width (w_{fy}) and depth (w_{fz}) do not introduce gauge-length mis-measurement errors. Furthermore, shifting the position of the flags on the specimen relative to the coordinate system origin introduces no gauge length error.

The specimen may also experience in-plane bending, in which the specimen deforms in the plane defined by the specimen head. As the specimen bends toward the scan, for example, the back edge of the top flag and the front edge of the bottom flag move up and forward. The l_{tt} -

¹ The distance between the top edge of the bottom flag and the bottom edge of the top flag.

Figure 4: Apparent gauge lengths and flag widths for in-plane bending.

defined gauge length changes, and the width of the flag seen by the laser extensometer increases. The same formalism for deformation as developed for the out-of-plane case may be used. For brevity, we will present only the results. Unlike the previous case, the depth of the flag (w_{fz}) and the position of the flags along the gauge length influence the gauge length mis-measurement. Figure 4a shows the apparent gauge length, again assuming the default values shown in Table 1, as a function of bending radius. The family of curves corresponds to the apparent gauge length as the center-point of the true gauge length moves from moves from 1.5 mm below the geometric center of the specimen to 1.5 mm above the geometric center. (For a 10 mm gauge length, when the upper flag is attached at 5 mm, the flags are centered about the coordinate system origin) The mis-measurement of the gauge length is not as severe as in the out-of-plane bending case. Figure 4b shows the width intercepted by the flag for the same flag positions as in Figure 4a. Small amounts of bending result in large changes in the intercepted width of the flag. Figure 4c shows the apparent gauge length for different flag depths (w_{fz}) at a constant 2 mm offset from the geometric center of the specimen. When the flags are placed symmetrically about the center point of the specimen, the apparent gauge length is independent of flag depth. Finally, Figure 4d shows that the intercepted width of the flag also increases with increasing flag depth (w_d) when the flags are displaced from the geometric center of the specimen.

Flag Revolution Without Bending

Figure 5: Schematic showing how the rotating flags intercept the laser scan.

Dramatic gauge-length measurement errors occur when one or both flag revolve about their axes during the test. This is perhaps the source of the largest potential error to the strain measurement. Figure 5 illustrates this revolution. In this view the flags are seen end-on. The shaded region represents the scan of the laser beam. The unshaded regions correspond to the dark areas where the flags have blocked the beam. The upper flag illustrates a clockwise rotation, whereas the lower flag illustrates a counter-clockwise rotation. The center of the flag rotation is dependant on the direction of rotation and the thickness of the flag attachment flange (w_{fa}). The position of the upper and lower corner of the flags, which define the l_{bb} and l_{tt} lengths will follow the equation of a circle whose radius is the distance from the relevant corner to the center of revolution. For a clockwise revolution, the lower edge of the flag moves down, relative to the center of rotation according to the following relation:

$$y_l' = w_{fy}(1 + (w_{fz}/w_{fy})^2)^{1/2}[\sin(-\tan^{-1}(w_{fy}/w_{fz}) - \psi)]$$

where ψ is the revolution angle. For a counter-clockwise revolution the upper edge moves up and the lower edge moves down according to the following relations (respectively):

$$y_u' = (w_{fz}^2 + (w_{fy} - w_{fa})^2)^{1/2}[\sin(\tan^{-1}(w_{fa}/w_{fz}) + \psi)]$$

$$y_l' = (w_{fy} - w_{fa})\cos(\psi)$$

Figure 6 shows the width of the flag as measured by the laser extensometer as a function of the flag revolution angle, ψ , assuming a flag width (w_{fy}) of 2 mm, and flag depth (w_{fz}) of 2 mm. Clearly, for very small revolution angles, flag thickness changes are large relative to the typical extensions measured during creep of ceramics, which are typically 100 μm . This change in width of the flag intercepting the laser scan produces an apparent change in gauge length. Figure 7 shows the worst-case scenario for this behavior, assuming a 10 mm gauge length and 1 mm flag width at the attachment point (w_{fa}). One flag revolves (in this case the top flag, counter-clockwise), while the other remains

Figure 6: Measured flag thickness as a function of flag revolution angle.

fixed. In this scenario, the two length measurements provide different values for the apparent gauge length, both of which are larger than the true gauge-length. The example shows a positive apparent strain, however for a flag revolution in the opposite direction, an apparent negative strain would be measured. If both flags revolve in the same direction at the same rate, the net effect is zero. The l_{bb} and l_{tt} measurements are the same, with no apparent strain. If both flags revolve in opposite directions at the same rate, l_{bb} and l_{tt} are the same, but an apparent strain will be measured. This effect occurs because the flags, due to the slot cut for attachment, have different centers of revolution for the different directions of revolution (see Figure 7). If both flags revolve at different rates (regardless of the direction), l_{bb} and l_{tt} will be different, and an apparent strain will be measured. However the difference is less than the case where a single flag revolves.

Horizontal Translation of Non-parallel Flags

Up until this point, we have assumed that the flags are placed on the specimen such that they are parallel to each other. When the flags are not parallel, they may introduce two types of error. The first is an absolute mis-measurement of the gauge length, to which we will return later. The second occurs if there is the possibility that loading train shifts relative to the laser scan during the course of the experiment.

Figure 7: Measured gauge length as a function of flag rotation for the case of the upper flag rotating counter-clockwise and lower flag fixed.

Our observations of actual specimens and measurements of the widths of the attachment slots of the flags (w_{fs}) lead us to believe that the flags may hang at angles between 0° and 20° . Figure 8 shows that the gauge length might change by up to $10\text{ }\mu\text{m}$ for lateral shifts of only $200\text{ }\mu\text{m}$ when the flags differ in attachment angle by as little as 3° . Since the typical strain-to-failure for creep-resistant silicon nitride is only about $100\text{ }\mu\text{m}$, this apparent length change might introduce strain measurement errors of about 10%. Presently, we have no estimate as to what reasonable shifts of the loading train relative to the laser scan might be, though.

Uncertainty Errors

The second class of mis-measurement errors comes from uncertainties in the gauge lengths caused by the nature of the measurement itself, rather than by deformations of the specimen. They first appeared above, in the discussion of changes in apparent gauge length caused by lateral translation of the loading train relative to the laser scan. When the flags hang at different angles from the specimen ($\phi_u \neq \phi_l$), they do not accurately reflect the specimen's true gauge length. Even slight deviations from absolute parallelism may introduce non-negligible errors into the gauge length measurement. Figure 9 shows the apparent gauge length produced for typical values of

Figure 8: Apparent gauge length change caused by horizontal translation of non-parallel flags.

ϕ_l , the angle the lower flag makes with the specimen, while holding ϕ_u constant at 5° . The gauge length error can approach 5% for nearly undetectable variations in the flag attachment angles.

A potentially more serious problem is the uncertainty in the actual flag attachment point itself. As shown in Figure 1, the flag contacts the specimen at two points, both of which lie within the creeping section of the specimen. To a first approximation, neglecting dimensional change of the specimen during creep, these two points on the flag cannot remain rigidly attached to the specimen surface during creep, as the volume between the two points is extending due to creep. As a result, only one of the points may remain rigidly attached to the specimen; the other must slide. The length of specimen producing the increasing separation of the flags may be as much as $l_g + w_{af}$ or as little as $l_g - w_{af}$, assuming parallel flags attached with $\phi = 0$. The former case corresponds to that where the outermost points remain attached during creep, while the latter corresponds to the case of the inner points remaining attached to the specimen. For reasonable choices of the values ($l_g = 10$ mm and $w_{af} = 1$ mm), this uncertainty is $\pm 10\%$ of the true gauge length.

Effect of Errors on Measured Creep Strains

To summarize the effects of some of these uncertainties, it is instructive to consider a "simulated" creep curves to which the effects of specimen bending have been added. Figure 10 shows such a calculation

Figure 9: Apparent gauge length as a function of lower flag angle, ϕ_l for non-parallel flags.

done for a representative creep curve for NT154 Si_3N_4 at 100 MPa and 1430°C ($t_f = 200$ h, $\epsilon_f = 0.007$). The figure shows two pairs of simulated creep curves for bending to a final radii of curvature of 5000 mm and 1000 mm. Since the simulation models "out-of-plane" bending, each simulation results in two curves: one in which the apparent strain is larger than the true strain and one in which it is less, corresponding to bending away from, and toward the laser scan, respectively. The simulated creep curves are calculated by assuming that the "rise-displacement" caused by "out-of-plane bending" increases linearly with time. The other important variables used in the simulation are typical for our experimental set-up and are as follows: $l_g = 10$ mm, $l_o = 5$ mm, $w_{fy} = 2$ mm, and $\phi_u = \phi_l = 0^\circ$. Clearly the strain errors are potentially very large, although the specimen bent to a 5 m radius of curvature shows only a 10% error in measured strain.

Fortunately, our experimental experience leads us to believe that we do not experience such large amounts of bending. In tests on these loading frames with similar specimens, Carroll *et al.* [1] found maximum bending radii of 17 m in crept specimens. In addition, the cavity volume fraction in crept specimens of both NT154 [9] and GN10 increase linearly with strain. Figure 11 shows this linear relation between failure strain and cavity volume fraction for specimens of GN10 Si_3N_4 all deformed at 1275° and 137.5 Mpa. Since the cavity volume fraction is a natural consequence of the deformation process, it acts as a second

Figure 10: Simulated creep curves for samples which bend to a 1 m radius of curvature during creep.

measure of the total strain to failure. If bending produced creep strain errors of the magnitude that Figure 11 implies, this linear dependence would not be possible, since it would be equally likely for the apparent strain to larger than the true strain than smaller. The variability from the best fit line in Figure 11 indicates that a maximum bending radius on the order of tens of meters is possible. Further work is in progress to examine the shapes of specimens before and after creep to ascertain the actual sample deformation induced by creep.

Figure 11 Failure strain vs. cavity volume fraction for GN10 Si_3N_4 specimens deformed at 1275°C and 137.5 MPa.

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3.5 NONDESTRUCTIVE EVALUATION DEVELOPMENT

Nondestructive Characterization

D. J. McGuire (Oak Ridge National Laboratory)

Objective/scope

The purpose of this program is to conduct nondestructive evaluation (NDE) development directed at identifying approaches for quantitative determination of conditions (including both properties and flaws) in ceramics that affect the structural performance. Those materials that have been seriously considered for application in advanced heat engines are all brittle materials whose fracture is affected by structural features whose dimensions are on the order of the dimensions of their microstructure. This work seeks to characterize those features using high-frequency ultrasonics and radiography to detect, size, and locate critical flaws and to measure nondestructively the elastic properties of the host material.

Technical progress

Ultrasonics - W. A. Simpson, Jr., and K. V. Cook

We continue to explore uses for our new very high-frequency (2-GHz) acoustic microscope. We previously demonstrated¹ the imaging of cracking in silicon nitride produced by diamond pyramid indentation and the presence of what may be residual stress surrounding a 70- μm pore introduced into alumina by seeding the powder with polydivinyl benzene styrene spheres. Natural porosity of less than 1 μm could also be seen in this image. Imaging of the residual stress pattern is not yet definitively established, as other possibilities for the origin of the observed pattern exist. For instance, diffusion of the sphere material into the alumina matrix might reasonably be expected to alter the elastic properties in the vicinity of the pore, which in turn would affect the acoustic image. Presumably, this possibility could be checked from a knowledge of the diffusion coefficient for the sphere material in alumina at the firing temperature. We do not have this information, however, and have not yet been able to determine if a model exists for transport of various organics in an alumina matrix.

A second possibility for the observed pattern surrounding the pore is diffraction of the acoustic surface wave by the pore boundary. This possibility was suggested by S. Satish at NASA Langley, who pointed out that the behavior of the image with transducer-to-sample distance, i.e., the $V(z)$ response, would then be just that expected from the Rayleigh wave velocity.

The imaging of residual stress is of more than academic interest. The importance of residual stress in the failure of ceramics is well known; presently, this property is determined either by destructive techniques or by such nondestructive approaches as X-ray diffraction. The latter is both expensive and time consuming, however, and also requires extensive safety procedures to guarantee the safety of test personnel. High-frequency acoustic microscopy, on the other hand, is rapid, simple to apply, and biologically innocuous.

We recently obtained a second indication of possible detection of residual stress using acoustic microscopy. A polished silicon nitride sample was scratched using a

diamond stylus under several loads. At the lightest load, the scratch was clearly discernable (to the acoustic microscope), but no cracking in the surrounding material was detected. At a critical load, however, cracks radiating from the scratch began to appear. With increasing load, the cracking became more evident, and transverse cracking in the bottom of the scratch was detected. Figure 1 shows the result obtained at 1 GHz and a magnification of 125 $\times$. Three scratches can be seen, and the increasing width of the scratches from left to right is indicative of the increasing stylus load. Cracks can be seen radiating into the surrounding silicon nitride, predominantly from the right side of each scratch. The reason for this asymmetry is not known although several causative factors can be suggested. On the rightmost scratch, a crack below the center of the scratch is seen to be bifurcated. The legends on the figure have low contrast because they are in color, and the figure is reproduced in black-and-white.

YP-18413

Fig. 1. Ultrasonic image at 1 GHz and 125 $\times$ of cracks and possible residual stress produced by scratching the surface of a silicon nitride block.

The most interesting characteristic observed in Fig. 1, however, is the banding parallel to each scratch. Although we have not established this conclusion by independent means, we believe the banding to be attributable to loading-induced stress. One observation which supports this hypothesis is the "streaming" of light and dark areas from the tips of the cracks. If the phenomena were caused solely by diffraction of the surface wave at the edge of each scratch, the bands would be affected only in the immediate vicinity of each crack. Another possible explanation is that of surface deformation induced by scratching. This cause can be supported or eliminated by surface profilometry, and we hope to obtain this confirmation shortly. However, it is difficult to envision how the surface could be distorted in such a manner as to produce the "streaming" evident in the figure.

Figure 2 is an acoustic image of the bottom of one of the scratches obtained at 1.2 GHz and a magnification of 625 $\times$. The fine, linear dark lines running across the scratch are transverse cracks. For this figure, the transducer was focused on the bottom

YP-18411

Fig. 2. Ultrasonic image at 1.2 GHz and 625 $\times$ of transverse cracking in the root of a scratch in silicon nitride.

of the scratch, and the thicker, parallel dark lines on the left edge of the scratch and below center are out-of-focus cracks higher up on the curved side of the scratch. The lighter nature of some of the cracks suggests that they are subsurface. A faint "streamer," one of those seen so well in the previous figure, can be seen in the left half of the picture extending from near the center to the lower left edge of the figure. The areas adjacent to the scratch appear very dark here because they are out of focus.

As we mentioned above, surface upset or depression would also produce the "banding" observed in the silicon nitride tribology sample, but the "streaming" of the banding around cracks would be very difficult to explain using this mechanism. We have now also examined a stainless steel single crystal which had been scratched in a manner similar to the ceramic specimen. The data showed a similar banding parallel to the scratch but no "streaming" in the region around the cracks, which followed crystallographic planes. Surface profilometry on this sample indicated a surface upset of several micrometers adjacent to the scratch. Using this information, we were then able to observe the upset by adjusting the focus of the microscope while operating in the line-scan mode (repetitive scanning of a single line), in effect performing acoustic surface profilometry. In this manner, we have learned to distinguish surface upset, which should help in the interpretation of future data.

We have also examined a scratched specimen of silicon carbide. Figure 3 shows the data obtained on one of the scratches induced by a diamond stylus. Both qualitatively and quantitatively, the data resemble that obtained on silicon nitride. Note the matrix cracking in the region adjacent to the scratch and the "banding" running essentially parallel to the crack. In addition, the same "streaming" of the band pattern can be seen flowing away from the vicinity of cracks. Unfortunately, this specimen was characterized before we realized that the microscope could be used to perform acoustic surface profilometry on the scratches, and we still do not know definitively whether the observed patterns may be attributed to surface upset or induced stress. We intend to have surface profilometry performed on both this specimen and the previous silicon nitride sample, but we believe that the results will show that the observed "streaming" pattern is not caused by surface deformation.

Figure 4 shows the acoustic results obtained at 1.2 GHz in the root of one of the scratches in silicon carbide. The presence and appearance of transverse cracking appear to be identical to that seen in silicon nitride. The very dark features are surface cracks which could also be seen visually. The fainter transverse lines are near- or sub-surface cracks which could not be seen optically. In addition to the cracking, longitudinal scratches can also be seen running along the root of the much larger diamond scratch.

Through S. Satish at NASA Langley, who has an instrument similar to ours (without the image storage and analysis hardware and software), we have learned that the motion of the acoustic transducer can be stopped via a keyboard command. This feature is undocumented in the manuals supplied with the instrument and is extremely useful in that it allows the transducer to be focused while stopped, thus minimizing lens damage should the transducer contact the sample surface during focusing, an event which is extremely easy to produce. At operating frequencies above 800 MHz, the lens-to-sample clearance at focus is only 30 μm . Because the instrument operates in a tone-burst (quasi-monochromatic) mode at these frequencies, the sample response goes through successive maxima and minima as a result of interference between direct and surface wave components as the lens-to-sample distance is altered. It is tempting to proceed too far during focusing in order to determine the optimum focal point, thus causing the lens to

Fig. 3. Acoustic image at 1 GHz of scratch-induced cracking and possible induced stress in silicon carbide.

strike the sample surface. Because of the very high hardness of ceramics, the potential for lens damage when this occurs is large.

We continue to receive requests from commercial vendors for assistance in evaluation of their products. One such request involved ceramic spark plug bodies which had failed high-voltage testing. The failed units contained small through-wall holes produced by electrical discharge. Of interest was the path through the ceramic taken by the discharge and the conditions (e.g., increased sample porosity) which existed in the failed region. The cross-sectional area of the plug body varies considerably along its length, and failure may occur at any point. Two samples were obtained. In the first sample, failure occurred in the thinnest region of the body and in the second near the thickest region. Both regions of failure were characterized by tiny, visible pinholes on the exterior surface of the sample.

The samples were examined ultrasonically using a 75-MHz focused transducer. In view of the fact that the material was a relatively porous alumina, retrospection suggests that a lower frequency may have yielded adequate results. We are considering repeating our examination at a frequency of 25 MHz.

Fig. 4. Acoustic image at 1.2 GHz of transverse cracking in the root of a scratch in silicon carbide.

Figure 5 shows the result obtained on the failure region located in the thin section of a plug body. Part of the punch-through discharge hole can be seen at the bottom of the figure, near the 7 o'clock position (the exit hole is located at the 6 o'clock position, but the path of the discharge through the ceramic is often quite tortuous). Since this is a flaw test, pores or discontinuities in the ceramic will appear as brighter regions. The very bright indication at about 1 o'clock on the inner surface of the sample is an artifact; it was produced by a standing-wave signal generated in the transducer lens getting into the data gate in this area of the scan. However, the bright indication at about the 2 o'clock position of the figure and about one-third of the way through the wall thickness is real; it is an unusually large pore.

The most striking feature of Fig. 5 is the apparently radial orientation of the internal structure of the ceramic. At all azimuthal locations around the cross section, the ultrasonic pattern suggests radially oriented structures. We have not seen this type of pattern previously; it may presumably be attributed to the fabrication process for the ceramic and should be of considerable interest to the vendor.

Figure 6 shows the flaw test results obtained on the second plug body sample. Note the areas of increased porosity (brighter) in the region from about 1 to more than

Fig. 5. Ultrasonic image of internal structure of a failed ceramic spark plug body showing radial features.

3 o'clock and around 8 o'clock in the figure. In addition, large pores can be seen at several locations around the figure, including a radial string of pores at about the 4 o'clock position. However, none of these features correlate with the location of the sample failure, which occurred at about the 6 o'clock position and is not seen. It is evident from these results that the pore distribution in this material is quite inhomogeneous.

We have also received some fabricated flaw standards in silicon nitride for evaluation of our flaw detection sensitivity. We have examined laser-drilled standards before, but none with such carefully controlled properties, range of depths, and excellent matrix density. These current standards consist of laser-drilled holes 25 and 50 μm in diameter whose bottoms lie at depths ranging from 0 to 5 mm. The standards were produced by counter drilling a 3-mm-diam pedestal to various depths and then laser drilling the flaw standards an additional 1 mm. The pedestal thus serves as a convenient target with which to locate each laser-drilled hole.

For those holes located within 125 μm of the surface, detection was accomplished with a high-frequency (50-MHz) surface wave. To our surprise, even the 25- μm flaw could

Fig. 6. Ultrasonic image of inhomogeneous porosity (brighter areas) in a failed ceramic spark plug body.

be detected at this depth by the surface wave. At 50 MHz, the wavelength of the acoustic surface wave is about 120 μm ; thus, the flaw, which is only about 0.2 wavelengths in diameter, is being detected at a depth of more than a wavelength. A second possibility is that the flaw is being detected, in part, by the refracted longitudinal-wave field of the surface-wave transducer; this remains to be checked.

For those flaw standards deeper than 125 μm , detection was accomplished using focused transducers ranging in frequency from 50 to 100 MHz. At the time this is being written, we have detected and imaged all the flaws to a depth of 3 mm, including the 25- μm standards. As the data look similar for all the standards, we present only those for a pair of flaws located at a depth of 3 mm. Figure 7 shows the enhanced results for a 25- and 50- μm pair 3 mm deep. The area scanned was 4 by 6 mm, and a 100-MHz, 25-mm focused transducer was used. The arrow indicates the 25- μm flaw, while the larger circular white area near the bottom of the figure is the 50- μm flaw. A few stepper-motor-induced noise pulses, which occur because of the very high gain employed to acquire the data, can also be seen near the left and right edges of the scanned area.

Using less enhancement, areas of increased scattering (relative to the background microstructural scattering) could be seen surrounding the images of the two flaws. These

Fig. 7. Enhanced ultrasonic image of a 25- (arrow) and 50- μ m flaw 3 mm deep in silicon nitride.

areas are undoubtedly clusters of pores much smaller than the 25- μ m flaw indicated by the arrow. The weakness of this scattering indicates that this is one of the densest and most noise-free ceramics we have examined.

We will continue to evaluate the deeper flaw standards as time permits. We anticipate that those flaws deeper than 3 mm (and smaller than 50 μ m) will present considerable difficulty, as we have repeatedly indicated in past reports. We may also examine these flaws using our synthetic aperture algorithms, although the counter-drilled pedestals present huge targets which will tend to interfere with the tiny flaw signals.

We continue to examine measurement of the nonlinear behavior of ceramics as a possible tool for characterization of the global state of damage. We are considerably hampered in this effort by lack of a suitable high-power tone-burst exciter for the ultrasonic transducer. Our present arrangement, which uses a gated oscillator and separate power amplifier, limits the peak transducer excitation to 100 V when operating properly. Unfortunately, instabilities in the amplifier further reduce the maximum useable excitation to 60 to 70 V, which makes detection of the second harmonic component in thin samples virtually impossible. We are trying to obtain a suitable high-power source on temporary loan but have not yet located such a unit.

Despite the problem of insufficient driving power, we have obtained a weak second-harmonic response in fused silica using low-power tone-burst (monochromatic) hardware which we possess and a lock-in amplifier capable of locking on the second harmonic of the reference frequency. Fused quartz was chosen as an initial target material primarily because the nonlinear parameter³, β , is relatively large and has been reported in the literature. To our knowledge, no values of the nonlinearity parameter have been determined for ceramics. Since the nonlinear response of any material increases quadratically with the driving voltage,³ it is crucial to use as much input power as possible. The current hardware limitation mentioned above is too low for accurate determination of the nonlinear response of the ceramics which we have examined so far, but higher levels of excitation should yield the expected anharmonicity.

Computed Tomography (CT) - B. E. Foster

As a part of our cooperative program for process equipment, several experimental, unfired Si_3N_4 gelcast samples were received from the ORNL Ceramic Processing Group for CT evaluation in June 1993. Three samples approximately 17 mm diam by 55 mm long were identified as Nos. 4, 6, and R86; one sample was approximately 30 mm diam by 55 mm long; one sample was approximately 30 mm diam by 80 mm long and was noted as having the binder removed; one rectangular sample identified as Denka 9S was approximately 10 × 22 × 98 mm. In addition, there were two fired Si_3N_4 samples, 12 mm long, identified as Nos. 001 and 002 with respective diameters of 6.25 and 12.5 mm and three fired SiC samples 12 mm long, identified as Nos. 006, 007, and 008 with respective diameters of 6.25, 12.5, and 25 mm. In total, there were six unfired and two fired Si_3N_4 samples and three fired SiC samples.

Initial CT scanning was accomplished and reported in the bimonthly report for June-July 1993. There were several linear and void-like indications noted in the CT scans that could have been associated with reconstruction artifacts. Verification of the existence of these indications was to be accomplished with subsequent scans at different rotational positions with the SUN workstation and new software. Two of the samples have been rescanned at several orientations and the indications verified. These indications have been verified with scans made at Scientific Measurement Systems on their CT scanner and subsequent scans at ORNL after installation of the SUN workstation in August 1993.

The verification of the indications in the remaining samples has been delayed by a very annoying intermittent failure of the microVAXII computer. Sometimes, the system would successfully reboot within the hour. At other times, the unit had to be powered down, then back up, left with the power "ON" overnight, and then successfully rebooted the next day. Initially, it was thought that the problem was associated with the computer processing unit (CPU) board or memory board. These were replaced by SMS, and the system worked fine for about 36 h, then failed. The boards that were removed worked fine in equipment at SMS. SMS then contracted for the Technical Representative of Digital Equipment Corporation (microVAXII manufacturer) who was located at ORNL to try to resolve the problem. Again, the CPU and memory boards were replaced, as well as other boards in the system, and the unit still failed.

The only items left to be replaced were the custom-designed Backplane and the multivoltage high-current power supply fabricated by PMC Associates. The power supply was a long lead time item (3 to 4 weeks) requiring return of the existing supply to PMC to ensure precise matching of unit size and sizes and locations of the multiple connectors.

This would have required complete shutdown of the equipment during that period. The backplane could be obtained and installed in about 1 to 2 weeks. The decision was made to install the backplane first. This was accomplished during the week of November 8. The unit immediately became operable, but the intermittency problem had to be checked for resolution. The decision was made to leave the equipment on during travel to American Society of Mechanical Engineers Code week. If the unit did not reboot and continued operation during early December 1993, the problem would be considered solved. If there was a single failure during that time, the plan was to ship the existing power supply to PMC for rebuild during the last three weeks in December and first two weeks in January 1994 covering vacation and holiday period.

Fortunately, the installation of the new backplane solved the very perplexing problem. The failures had also impacted the ability to evaluate the new version of the 3-D Solid Program. SMS installed an operable version of this software in January 1994.

As a part of our cooperative program for process equipment, six alumina samples (spark plug bodies) that had failed during testing were received from the ORNL Ceramic Processing Group, and two diamond-coated grinding wheels (one of which had failed during use) were received from the ORNL Ceramic Surface Systems Group for CT evaluation.

The failure of the spark plugs occurred during testing which consisted of inserting a metal probe and energizing it with 25,000 V. The arc passed through the wall of the plugs. The size of the hole through which the arc passed varied from plug to plug, as can be seen in Figs. 8 and 9. The pinhole in one of the plugs can be seen near the bottom of the CT slice in Fig. 8. Figure 9 shows a CT slice from a different plug and a much larger hole in the wall. Approximately 20 CT slices at 0.25-mm increments were taken to trace the hole from I.D. to O.D.

Figure 10 shows a CT slice from a diamond-coated grinding wheel (15 cm diam by 1.2 cm thick) with a phenolic core. At the 7 o'clock position, a circumferential linear indication is visible at the interface of the coating layers. Similar indications were noted at the 4 and 12 o'clock positions. Figure 11 is a CT slice from another diamond-coated grinding wheel (18.5 cm diam by 1.5 cm thick) with a core containing a large amount of copper. This wheel had failed and part of the diamond coating had fallen away. Note the crack-like indication below the chipped area between the coating and core. In addition, there are two linear indications that can be seen in the core at about the 7 o'clock and 4 o'clock positions. Other circumferential linear indications were noted between the layers of the coating.

Our plan now is to scan additional used grinding wheels for characterization of the indications being found. Then, some new wheels will be evaluated with follow-up testing after use and perhaps subsequent failure in an attempt to identify the cause of failure.

Three experimental exhaust manifolds were received for CT evaluation. They were identified as samples 1, 2, and 3. Each sample had an inner cylinder of ceramic with a wall that was approximately 6 mm thick. This cylinder was wrapped with a compliant layer of some material unknown to us and then cast with an outer layer of cast iron that was about 12 mm thick. Figures 12 through 14 show a single CT slice of each of the respective samples. In Figure 12, the porosity in the compliant layer is very obvious, as well as the penetration of the cast iron (white area) through the compliant layer to the ceramic cylinder at the 3 o'clock position. It was noted that each time the cast iron penetrated the compliant layer and contacted the ceramic, there was cracking in the ceramic. The compliant layer in Figure 13 is significantly less porous. In Figure 14, the

Fig. 8. CT slice (0.25 mm thick) of the spark plug sample No. 1B.

porosity in the compliant layer is again obvious. Note the penetration of the cast iron through the compliant layer to the ceramic cylinder at the 9 o'clock position. The ceramic wall was cracked in that region.

In addition, an experimental ceramic rotor and a silicon nitride turbine blade was received for evaluation. The next two figures are included to show some of the capability available with the SUN workstation. Figure 15 shows a solid 3-D reconstruction using 45 CT slices of the ceramic rotor. Once the slices are obtained, reconstructions in different vertical positions can be accomplished without rescanning. Also, the digital image can be rotated to view any and all surfaces quite rapidly.

Figure 16 shows the solid 3-D reconstruction using 115 CT slices of the turbine blade. A cracklike indication that was noted in one of the slices immediately above the base platform was also visible when a vertical reconstruction through the 115 slices was accomplished.

Milestones

On schedule.

Fig. 9. CT slice (0.25 mm thick) of the spark plug sample No. 1E.

Publications

A paper entitled "Applications of Scanning Acoustic Microscopy in Analyzing Wear and Single-Point Abrasion Damage" by P. J. Blau and W. A. Simpson, Jr., has been prepared for the *Wear of Materials '95* Conference to be held in Boston, Massachusetts, April 3-6, 1995.

References

1. W. A. Simpson, Jr., "Nondestructive Evaluation Development," *Ceramic Technology Project Bimonthly Technical Progress Report*, August-September, 1993, p. 74.

Fig. 10. CT slice (0.5 mm thick) of the diamond-coated grinding wheel with a phenolic core.

2. W. A. Simpson, Jr., "Nondestructive Evaluation Development," *Ceramic Technology Project Bimonthly Technical Progress Report*, October-November, 1993, p. 59.
3. W. A. Simpson, Jr., "Nondestructive Evaluation Development," *Ceramic Technology Project Bimonthly Technical Progress Report*, June-July, 1993, p. 69.

Fig. 11. CT slice (0.5 mm thick) of the diamond-coated grinding wheel with copper in the core.

Fig. 12. CT slice (0.5 mm thick) of the exhaust manifold sample No. 1.

Fig. 13. CT slice (0.5 mm thick) of the exhaust manifold sample No. 2.

YP-19151

Fig. 14. CT slice (0.5 mm thick) of the exhaust manifold sample No. 3.

Fig. 15. Solid 3-D reconstruction (using 45 CT slices, 0.25 mm thick) of an experimental ceramic rotor.

Fig. 16. Solid 3-D reconstruction (using 115 CT slices, 0.25 mm thick) of an experimental silicon nitride turbine blade.

X-ray Computed Tomographic Imaging – W. A. Ellingson, E. A. Sivers, D. L. Holloway (Argonne National Laboratory), in cooperation with J. P. Pollinger and H. C. Yeh (Allied Signal Ceramic Components)

Objective/Scope

The objectives of the Phase III work in this project are to (1) utilize 3-D X-ray micro-computed tomography techniques to study density distributions in composite green-state (as-cast) pressure-slip-cast ATTAP rotors, and (2) correlate destructive density analysis (to be conducted by Allied Signal Ceramic Components) of the as-cast ATTAP rotors with the 3-D X-ray microtomography density data.

Technical Highlights

This period, we received the step-wedge (Milestone 3.5.1.5.11) and our first rotor (Milestone 3.5.1.5.13).

ATTAP Rotor Density Studies

We obtained X-ray attenuation data on the Si_3N_4 step-wedge and have processed the data to obtain beam-hardening data for the first ATTAP rotor. The procedure involves measuring the attenuation for each step and plotting it against the thickness of the step. If the X-ray source were monochromatic, the plot would be a straight line. Specifically, if the initial X-ray intensity is I_0 , the linear attenuation coefficient of Si_3N_4 is m , and the path length in the wedge is x , the transmitted intensity I will be given by

$$I = I_0 e^{-mx} \quad (1)$$

Taking the negative of the natural logarithm of both sides yields the attenuation, mx , as

$$mx = \ln(I_0/I) \quad (2)$$

Because the source is actually polychromatic, the relationship between I and I_0 is nonlinear. A single-material beam-hardening correction consists of building a lookup table to yield a linear correction. The slope of the straight line (monochromatic energy chosen) is arbitrary, but is usually chosen to minimize the changes that must be made to the data because of noise considerations.

A schematic of the wedge used in this study is shown in Fig. 1. Each step was measured for its exact thickness (see Table 1). Figure 2 is a schematic diagram of the data acquisition setup used to obtain the step-wedge data, and Fig. 3 is a photograph of the setup. Figure 4 shows the ATTAP pressure-slip-cast rotor in place prior to data acquisition.

Table 1. Dimensions of step thicknesses

Step Number	Step Thickness (cm)
1	1.16
2	2.32
3	3.48
4	4.64
5	5.80
6	6.98
7	8.14
8	9.30
9	10.46
10	11.62
11	12.76
12	13.91

Fig. 1.
Schematic of
step-wedge.

Fig. 2.

Schematic diagram
of the data acquisition
setup used to obtain
the beam hardening
correction.

Fig. 3. Setup for step-wedge.

Fig. 4. ATTAP rotor in place prior to data acquisition.

Because we need to penetrate the rotor blades, all twelve steps of the step-wedge must be measured to cover the attenuation range of the ATTAP rotor. However, at the initial energy used (110 kVp), measurements of 11 steps revealed a drop in attenuation of $\approx 12150:1$ between air and the 12.761 cm (the eleventh) step. Because this exceeds the dynamic range

of our data acquisition system (which $\approx 500:1$), it was necessary to acquire data in five separate scans with increasingly long integration times for the thicker sections and to shield the image intensifier from air paths during the longer exposures. Each scan was taken twice, once with small, thick lead blockers partially blocking the beam to measure scatter, and once without. Dark current was also measured and removed. The system was not corrected for detector nonlinearity, but this is planned for the next measurement.

Figures 5-9 show horizontal row plots for each of the five data acquisitions. Figure 5, which shows the air scan with and without the lead blockers, was taken with an integration time of 25 ms. The dashed line is our estimate of the scatter in the regions that were not blocked. Figure 6, which shows a scan of steps 1-5 with and without lead blockers, was taken with an integration time of 330 ms. Figure 7, which shows a scan of steps 5-9 with and without blockers, was taken with an integration time of 1800 ms. Figure 8 shows a scan of steps 3-7 with and without lead blockers and was taken with an integration time of 4600 ms. Figure 9, which shows a scan of steps 7-11 with and without blockers, was taken with an integration time of 6000 ms. In each case, 101 data acquisitions were averaged to reduce noise. Data acquisition began at column 475 (of 1024), but the column intersecting the perpendicular to the source is 348, so that path lengths must be corrected for the angle of the fan beam. The source-to-detector distance is 91 cm and the pixel size is 0.0118 cm. We see from Fig. 9 that another scan is needed to measure steps 10-12 properly. For the thicker steps, the small difference in path length caused by the beam angle makes a large difference in attenuation.

Figure 10 shows the resulting beam-hardening curve. The choice of straight line was made to minimize the required changes to the data. The line shown has a slope of 1.269 and a RMS error of 1.098 and was chosen by minimizing the RMS error. The correction table will be made by recording the difference between the straight line and the curve for each value of $\ln(I_0/I)$ and adding it to actual data readings.

This analysis reveals that a scan of the rotor cannot be accomplished with a single scan using the present system. It is possible that a higher energy source (320 kVp) will shrink the difference somewhat between the attenuation of air and the attenuation of 14 cm of Si_3N_4 , but possibly not enough for the dynamic range of our system. We are currently developing a scanning method that combines several partial scans so that the integration time can be longer for the scan of the center of the rotor than for the outer regions.

Fig. 5. Effect of scattering on blank screen image intensity.

Fig. 6. Measured image gray scale as a function of step-wedge position for steps 1-5.

Fig. 7. Measured image gray scale as function of step-wedge position for steps 3-7.

Fig. 8. Measured image gray scale as a function of step-wedge position for steps 5-9.

Fig. 9. Measured image gray scale as a function of step-wedge position for steps 7-11.

Fig. 10. Resulting beam-hardening correction curve.

Nuclear Magnetic Resonance Imaging - S.L. Dieckman, S. Ahuja, O. O. Omatate,[#] A. C. Raptis, and W. A. Ellingson, Argonne National Laboratory; [#]Materials and Ceramics Division, Oak Ridge National Laboratory

Objective/Scope

The purpose of this work is to evaluate the potential of NMR imaging to affect the development and process control of near-net-shape gel-cast ceramic composites. Specific objectives of this work are to determine the utility of NMR imaging for (1) 3-D mapping of polymerization homogeneity; (2) real-time imaging of the polymerization process; (3) non-destructive evaluation of voids and flaws in the resultant components; and (4) measurement of physical properties such as degree of polymerization, viscosity, and specimen strength via correlation of these properties with measurable NMR parameters (T_1 , $T_{1\rho}$, and T_2). This work will be performed in conjunction with Dr. Ogbemi O. Omatate of the Materials and Ceramics Division at Oak Ridge National Laboratory.

Technical Highlights

NMR spectroscopic studies on the methacrylamide-N,N'-methylene bisacrylamide (MAM-MBAM) copolymer system have been conducted. The purpose of these studies is to provide the basic set of experimental parameters required for further NMR imaging. Such parameters include the appropriate pulse repetition rates, variations in chemical shift due to temperature and pH, and expected relaxation rates as a function of polymerization. We used Tecmag NMR Kit II and Libra data acquisition system that interacted with the CXP-100 Spectrometer and a Macintosh Quadra 950 computer. NMR images of spatial distribution of the standard MAM-MBAM (13.3 wt.% methacrylamide, 1.6 wt.% N,N'-methylene bisacrylamide, and 85.0 wt.% H₂O) copolymer premix without the initiator at a magnetic field strength of 2.35 T were conducted on an in-house-built probe tuned to the proton resonance frequency of 100.13 MHz. Orthogonal linear magnetic field gradients across the specimen were driven by three 1000-W Techtron audio amplifiers. The single-pulse sequence evolved an encompassing quasi-lorentzian signal due to various constituents of the premix, including the solvent. Figure 1 is a 2-D ¹H image of the MAM-MBAM copolymer premix. Here, polymerization has not begun because no initiator has been added to the premix. The image shows the concentration gradient in the specimen. It may be noted that the signal obtained is largely due to the solvent (H₂O) in the premix and has overwhelmed the signal from the other constituents present in the premix.

NMR images of the spatial distribution of the standard MAM-MBAM (13.3 wt.% methacrylamide, 1.6 wt.% N,N'-methylene bisacrylamide, and 85.0 wt.% H₂O) copolymer premix with the initiator were also obtained via the in-house-built probe. The signal obtained was largely due to the solvent (H₂O) present in the premix and overwhelmed the signal from the other constituents in the premix. Spectra were acquired with H₂O as the solvent at 25°C. The standard inversion recovery NMR pulse technique was employed to measure spin-lattice relaxation times, T_1 . A sequence of spectra were acquired with varying interpulse delay times (τ). The polymerization of MAM-MBAM copolymer mix due to the initiator was characterized by the changing T_1 's values of H₂O in the mixture. Figure 2 shows the sample configuration used in the experiments. The sample geometry was such that MAM-MBAM without the initiator was placed in a small inner tube (5 mm in diameter) immersed in a larger-diameter (15 mm) tube containing polymerizing MAM-MBAM (with the initiator). Figure 3 shows a sequence of 2-D ¹H images of the MAM-MBAM polymerization reaction with time. The sequence of images shows that due to polymerization, T_1 relaxation occurred more rapidly in the polymerizing MAM-MBAM (i.e., in the outer tube), while the inner tube T_1 remains constant.

Fig. 1. 2-D ^1H image of standard MAM-MBAM (13.3 wt.% methacrylamide, 1.6 wt.% N,N'-methylene bisacrylamide, and 85.0 wt.% H_2O) copolymer premix.

Fig. 2. Sample configuration (left) and probe assembly (right) used in imaging experiments.

Fig. 3. 2-D ^1H images at 0, 45, 80 and 140 min) of standard MAM-MBAM (13.3 wt.% methacrylamide, 1.6 wt.% N,N'-methylene bisacrylamide, and 85.0 wt.% H_2O) polymerization reaction with initiator.

Because the images are individually scaled in intensity, it appears that the inner tube intensity is decreasing. Figure 4 is a plot of image intensity variation as a function of time. The expected behavior has been indicated in Fig. 5 via a plot of intensity ratio (outside intensity/inside intensity, I_1/I_2) with time as the polymerization reaction occurs. Evidence of variation of T_1 with time during polymerization is given in Fig. 6. Variable-temperature studies on the same system have indicated that NMR is extremely capable of following the polymerization process.

Fig. 4. Intensity variation as a function of time, derived from polymerization images of MAM-MBAM copolymer mix.

Fig. 5. Plot of ratio of intensities of polymerizing MAM-MBAM (I_1) to uninitiated MAM-MBAM (I_2) with time.

Fig. 6. Variation of spin-lattice relaxation time, T_1 , with time during polymerization of MAM-MBAM (13.3 wt.% methacrylamide, 1.6 wt.% N,N'-methylene bisacrylamide, and 85.0 wt.% H_2O).

NDE Standards for Advanced Ceramics

R. W. McClung (Oak Ridge National Laboratory)

The development of standards is important for the establishment of reliability and acceptance of advanced structural materials. Committee C-28 on Advanced Ceramics is organized in the American Society for Testing and Materials (ASTM) to address this issue. One of the activities of the C-28 committee is nondestructive examination (NDE). The Task Group on NDE (TGNDE) is reviewing existing standards on NDE (primarily developed for metals) to determine potential applicability for ceramics as well as preparing original standards. Use of existing or modified standards is more efficient than generation of new documents and will ensure the input of a large body of NDE expertise. Close liaison is established with ASTM Committee E-7 on Nondestructive Testing, and documents are in various stages of review, recommendations for modification, and balloting. R. W. McClung is a member of both committees and the official liaison.

Liaison and technical support have been continued between ASTM Committees C-28 and E-7. To date, thirty-six E-7 NDE standards have been reviewed in detail with recommendations made to E-7 for modifications to identified documents. Successful action is complete on 31 documents; the others require action by C-28.

A new draft standard on "Ceramic Reference Specimens Containing Seeded Inclusions" was balloted concurrently at both subcommittee and committee levels (C28). The draft is being revised to accommodate comments received in the ballot process. A new draft standard for making precise measurements of ultrasonic velocity in advanced ceramics (one application is determination of porosity in ceramics) was balloted at the C28.02 subcommittee level. An advisory ballot was also conducted concurrently for information and technical comments in subcommittee E07.06 (on ultrasonic nondestructive testing methods). The draft standard on velocity is also being revised to accommodate comments received. A TG advisory ballot was conducted to obtain comments on the applicability of five recent E-7 standards. Four of the standards were approved as being applicable to advanced ceramics. These were E-1390, *Standard Guide for Illuminators Used for Viewing Industrial Radiographs*; E-1411, *Standard Practice for Qualification of Radioscopic Systems*; E-1441, *Standard Guide for Computed Tomography (CT) Imaging*; and E-1453, *Standard Guide for Storage of Media That Contains Analog or Digital Radioscopic Data*. The fifth standard, E-1324, *Standard Guide for Measuring Some Electronic Characteristics of Ultrasonic Examination Instruments*, was approved but comments were made relative to its limitation to frequencies of 25 MHz or less. Since some ultrasonic techniques for advanced ceramics require higher frequencies, a request will be made through liaison with Committee E-7 for modification to the standard to accommodate higher frequencies. Revision of C-1175, the standard guide for existing NDE standards, will begin to enter those newly approved. Further action is planned on requesting data for "radiographic equivalence factors" from members of the TG and other potential sources of data. Other work in progress includes an amplified outline for a draft standard for reference specimens containing laser-drilled holes and a possible standard on determination of porosity in ceramics using ultrasonic velocity. The latter standard will be delayed until the standard on ultrasonic velocity is completed. Preparation of a list of facilities and expertise for NDE of advanced ceramics at government laboratories is planned. A new International Standard Organization (ISO) Technical Committee (TC) 206 on Fine Ceramics has been established with Japan as the Secretariat and Sam Schneider (NIST) as chairman. McClung, as chairman of subcommittee C-28.02 on Design and Evaluation, is a member of the U.S. Technical Advisory Group (TAG) for TC 206. During the meetings of C-28, January 7-9, 1994, discussion was

held in meetings of the TAG, as well as subcommittee C-28.02, to establish recommendations for work items for the TC. It was recommended that the C-28 standards on NDE be submitted to the TC for the first organizational meeting to be held in Japan in May 1994.

During the meetings of Committee E-7, January 16-20, 1994, several liaison activities were conducted or reported. McClung also participated in the preparation and balloting of several standards with potential application to ceramics. During the meeting of the ultrasonic subcommittee, a verbal request was made for a modification to E-1324 (see above) to allow application at frequencies above 25 MHz (at least up to 100 MHz). This will be followed with a formal written request providing more details on the needed changes. McClung also met with the radiology subcommittee and requested modification to the CT document (E-1441 above) to clarify and simplify the sections on "Summary of Practice and Use." He agreed to participate with the task group by reviewing draft modifications. In Committee E-7, several documents are in progress on radiography, computed tomography, and ultrasonics with relevance for application to advanced ceramics.

4.0 TECHNOLOGY TRANSFER

4.1 TECHNOLOGY TRANSFER

4.1.1 Technology Transfer

Technology Transfer

D. R. Johnson (Oak Ridge National Laboratory)

Technology transfer in the Ceramic Technology Project is accomplished by a number of mechanisms including the following:

Trade Shows - A portable display describing the program has been built and has been used at numerous national and international trade shows and technical meetings.

Newsletter - A Ceramic Technology Newsletter is published regularly and sent to a large distribution.

Reports - Semiannual technical reports, which include contributions by all participants in the program, are published and sent to a large distribution. Informal bimonthly management and technical reports are distributed to the participants in the program. Open-literature reports are required of all research and development participants.

Direct Assistance - Direct assistance is provided to subcontractors in the program via access to unique characterization and testing facilities at the Oak Ridge National Laboratory.

Workshops - Topical workshops are held on subjects of vital concern to the ceramics community.

International Cooperation - This program is actively involved in and supportive of the cooperative work being done by researchers in West Germany, Sweden, the United States, and, most recently, Japan under an agreement with the International Energy Agency. This effort is ultimately aimed at development of international standards and includes physical, morphological, and micro-structural characterization of ceramic powders and dense ceramic bodies, and mechanical characterization of dense ceramics.

IEA ANNEX II Management

V. J. Tennery and K. Breder (Oak Ridge National Laboratory)

Objective/scope

The purpose of this task is to organize, assist, and facilitate international research cooperation on the characterization of advanced structural ceramic materials. A major objective of this research is the evolution of measurement standards. This task, which is managed in the United States by ORNL, now includes a formal IEA Annex agreement identified as Annex II between the United States, Germany, Sweden, and Japan. The original annex included four subtasks: (1) information exchange, (2) ceramic powder characterization, (3) ceramic chemical and physical characterization, and (4) ceramic mechanical property measurements. In the United States, a total of 13 industrial and government laboratories have participated and contributed their resources to this research. The research in subtasks 2, 3, and 4 is now complete. During CY 1990, agreements were reached for Japan to join the annex and for research in two new subtasks to be initiated. These include subtask 5, "Tensile and Flexural Properties of Ceramics," and subtask 6, "Advanced Ceramic Powder Characterization." The research in subtasks 5 and 6 is now complete, and the reports have been distributed.

Several matters were handled at the Executive Committee Meeting, held October 6, 1993, in Stuttgart, Germany. Belgium applied for membership in this task and should receive approval shortly by the Executive Committee. The lead representative from Belgium is Dr. Jean-Pierre Erauw of the Vlaamse Instelling voor Technologisch Onderzoek, Mol, Belgium. In addition, application for extension of Annex II to June 30, 1997, is being submitted to IEA Headquarters, Paris. Revisions to the annex and some other matters could not be fully resolved during the 4-h meeting, and these matters will be handled by the committee chairman by telefax, etc. New tasks, subtask 7, "Ceramic Machining and Surface Characterization," and subtask 8, "Ceramic Powder Characterization," were proposed in late FY 1993 and have now been accepted by all member countries. The meeting adjourned with the committee expressing thanks to the technical leaders in each subtask in each country.

Belgium has proposed to organize the 1994 IEA ANNEX II Executive Committee Meeting in Mol, Belgium, October 21, 1994, in conjunction with the 3rd International Ceramic-Ceramic Composites Conference in Mons, Belgium, October 18-20, 1994. It is very likely that this proposal will be accepted within the next month.

Technical highlights**Subtask 5, Tensile and Flexural Properties of Ceramics**United States

V. J. Tennery distributed the U.S. final subtask 5 report (20 copies) at the Executive Committee Meeting held in Stuttgart on October 6. The subtask 5 report was mailed to the participants on November 4, 1993.

Germany, Sweden, and Japan

Subtask 5

Germany distributed the following reports at the Executive Committee Meeting held in Stuttgart on October 6: (1) "Materials Research Program, Annual Report 1992, High-Performance Ceramics," presented by the Project Agency Materials and Raw Materials Research (PLR) Center, Jülich GmbH (copies sent to U.S. participants); and (2) "Mechanical Characterization of Engineering Ceramics, IEA ANNEX II Subtask 5," by A. Brückner-Foit, W. Berweiler, T. Holstein, A. Mann, D. Munz, and K. Schirmer, September 1993.

Sweden distributed the following report at the Executive Committee Meeting held in Stuttgart on October 6: "Priority Research Program, High-Performance Structural Ceramics in Sweden, 1987-1992, IEA Technical Report," September 1993 (copies sent to U.S. participants). Received on November 11, 1993, were five copies of the Swedish summary report on subtask 5 entitled "Mechanical Characterization and Fractographic Investigations of Silicon Nitride, IEA ANNEX II, Subtask V, Swedish summary report."

Japan distributed the following report at the Executive Committee Meeting held in Stuttgart on October 6: "Technical Report on Japanese 100-kW Ceramic Gas Turbine for Automobiles," Petroleum Energy Center, March 1993 (copies sent to U.S. participants). The summary report of subtask 5 research will be sent soon.

Subtask 7, Machining Effects on Strength of Structural Ceramics

ORNL has technical responsibility for this subtask. With the inclusion of Belgium as a full participant in subtask 7 and with Germany also participating fully, the number of countries in subtask 7 is five. Concerns were raised from several participants that the combined U.S./Japan research plan would involve a large number of specimens and be very costly. The manager of subtask 7, therefore, proposed in a letter to the participants that the plan be modified to essentially coincide with the original Japanese plan. This will include 270 specimens being machined in each country and 270 specimens being measured in each country, apart from any other internal specimen studies. In the United States, this internal work will include an additional 360 flexure specimens for a total of 630. This plan has been agreed to by all the participants. The work plan for subtask 7 is now fixed.

Belgium has agreed to the proposed work plan for subtask 7 (letter from Dr. Erauw, February 16, 1994).

The Federal Ministry for Research and Technology, BMFT, agreed formally to German participation in subtask 7 (letter from Drs. Faul and Seitz, February 2, 1994).

Japan agreed to the subtask 7 proposal (letter from Dr. Mizuno, February 16, 1994).

Sweden agreed to participate in subtask 7 (letter from Dr. Pompe, February 22, 1994).

A working group meeting for the international participants of subtask 7 will be held in conjunction with the American Ceramic Society 96th Annual Meeting, April 24-28, 1994, Indianapolis, Indiana, to discuss subtask 7.

United States

In an effort to select the most appropriate silicon nitride from the United States for the machining studies under subtask 7, five different high-strength silicon nitrides were ordered and machined into four-point flexure bars according to American Society for Testing and Materials (ASTM) C1161. The microstructures of the selected ceramics varied somewhat; some had a bimodal grain structure containing acicular grains to promote high toughness, while others had a uniform, small grain size. Forty specimens of each material were randomized and fractured at room temperature at a crosshead speed of 0.5 mm/min. The fixture was the same as used by ORNL in subtasks 4 and 5. Before and after the randomized set was fractured, the alignment of the fixture was checked and adjusted by inserting a strain-gaged specimen which was loaded to 70% of estimated fracture load. Strength results and Weibull parameters calculated by the maximum likelihood method are shown in Table 1. The remarkably high Weibull modulus (31) for material No. 1 is coupled with a very high strength. The accompanying fractography showed that the lowest strength specimen in this set resulted in fracture from an inclusion, while the rest of the fractures originated at the surface and near the surface from small irregularities in the microstructure interacting with the free surface.

Table 1. Strength and Weibull Parameters for the Five Silicon Nitrides

Material No.	Average strength (MPa)	Standard deviation	Weibull Scaling factor S_0	Weibull modulus m
1	1026.6	55.3	1046.2	30.9
2	890.9	80.1	926.0	13.9
3	848.8	54.2	873.4	18.9
4	756.4	75.9	789.8	11.5
5	565.5	64.4	593.5	9.9

An ANOVA analysis showed that the strength of material No. 1 was significantly larger than the strength of material No. 2 ($\alpha = 0.05$) and also that the variance was significantly different. The fractography showed that this ceramic, i.e., No. 2, failed from inclusions in the lower end of the strength distribution and possibly from other flaw types in the higher end of the strength distribution. Further fractography of these two materials and the three remaining materials is currently under way.

Following the determination of the relative strength and Weibull parameter comparisons for five silicon nitride ceramics, GS-44 material was selected because of its high characteristic strength and Weibull parameter α . Fourteen billets of GS-44 silicon nitride (102 x 102 x 122 mm) [4 x 4 x 0.5 in.] were ordered from AlliedSignal Aerospace Co., Ceramic Components, Torrance, California, on January 26, 1994, for use in the work in this subtask. Instrumentation of the surface grinder has been evaluated by cross

grinding a series of eight sets of flexure specimens under a range of grinding conditions. Preliminary analyses indicate that dramatic variations in both the Weibull shape parameter and the characteristic strength can be produced in this material with the instrumented machine to be used in producing the flexure specimens in this subtask. The GS44, Si_3N_4 billets to be used for flexure specimen preparation are expected to be shipped to ORNL by mid-May. Following preliminary grinding studies on reference billets in the HTML, a meeting of U.S. participants to finalize grinding parameters to be used is planned for mid-summer. Work has continued on characterization techniques for machined ceramic surfaces. A new laser profilometer and software for generating and analyzing machined surface maps has now been demonstrated in the HTML Ceramic Machining User Center and will be used in this subtask by the participants.

Germany, Sweden, and Japan

Subtask 7

No report this period.

Subtask 6, Advanced Ceramic Powder Characterization

Major responsibility for this subtask in the United States is at the National Institute of Standards and Technology (NIST), and a detailed report of progress on this subtask is provided in the section of this report submitted by NIST.

S. Malghan distributed the U.S. final subtask 6 report to the Executive Committee at the meeting which was held in Stuttgart on October 6. This report is expected to serve the participants highly effectively because it contains vital procedures and data for a number of powder characterization procedures for which repeatability and reproducibility data are available. In addition, the procedures are expected to serve in the standardization process on the international scale. The Executive Committee authorized the release of this report to the standardization committees in Japan, Europe, and the United States. This is considered to be a major step in assisting the ceramic powder characterization standardization programs in these countries. The subtask 6 final report was mailed to the participants on November 16, 1993.

Seven additional copies of the final subtask 6 report were sent to Dr. Makio Naito, Japan Fine Ceramics Center, at his request, for the standardization effort in Japan (March 21, 1994).

Subtask 8, Ceramic Powder Characterization

Major responsibility for this subtask in the United States is at NIST, and a detailed report of progress on this subtask is provided in the section of this report submitted by NIST.

The technical leaders of powders characterization subtasks met in Stuttgart, Germany, in conjunction with the IEA Executive Committee Meeting on October 6, 1993. S. G. Malghan made presentations to the executive committee to summarize the developments in the subtasks. The subtask 8 technical program has been finalized, and a number of parallel activities are in progress. The procedures collection and development is one of the most important tasks since very few procedures are available. A set of

preliminary procedures has been collected from the participants, and the rest are being developed at NIST. The primary activities during this period were on the development of procedures, analysis of participants' feedback, and collection of powders. We are continuing to develop, revise, and test procedures for characterization of secondary properties of powders. At present, we have several procedures that have been tested using alumina as a candidate powder. The A-16 alumina, one of the optional powders, is being used since it is readily available. The testing involves primarily the evaluation of major parameters affecting the robustness of the procedures and effects of the measurement parameters on the response. Some of the procedures that have undergone testing are deagglomeration by ultrasonication, settling behavior, and agglomerate size distribution in the measurement of dispersion. In addition, pH of slurry, sedimentation, and casting rate in the preparation of slurry have been tested.

Subsequent to the decisions at the Stuttgart meeting of technical leaders, a questionnaire was mailed to participants to seek their views on selection of a second silicon nitride powder in place of silicon carbide and inclusion of aluminum nitride as another optional powder. There is sufficient interest among the participants to include aluminum nitride as an optional powder. However, interest in substituting another silicon nitride powder for silicon carbide is not evident. This issue is being discussed with technical leaders.

Regarding the procurement of primary and optional powders, we need at least 25 kg each of these powders. Two of the five powders have been ordered. The rest will be purchased shortly.

During this period, we have been working on procedures and powders as related to the subtask 8 project. In one area of this project, we are continuing to improve existing procedures, draft new procedures, and collect additional procedures from participants. A procedure for the determination of agglomerates size distribution has been developed and tested at NIST. This procedure has been found to provide fairly repeatable data.

Technical leaders in Japan and Germany have held meetings with their participants to review progress and reach a consensus on powders selection and work distribution. Subsequently, Dr. Naito, Japan's Technical Leader, visited NIST to coordinate with the primary effort. During a week-long meeting, several subjects, including feedback from Japan's participants meeting, standardization activities in Japan, and preliminary comments on procedures, were discussed. A meeting of the U.S. participants will be held in May.

Inputs from a significant number of participants with respect to their selection of powders have been analyzed. It appears that all six powders proposed at the Stuttgart Executive Committee Meeting in Germany have been retained for study. In addition, the participants in Japan would like to study a number of primary properties of secondary powders (alumina, zirconia, and aluminum nitride). Dr. Naito has agreed to collect the procedures for analysis of primary properties of these powders.

A 25-kg batch of silicon nitride powder has been purchased from Ube Industries. In addition, samples of alumina and aluminum nitride powders have been provided by Alcoa and Dow Chemical Company, respectively. The zirconia powder will be supplied by Japan, while silicon carbide and gas phase silicon nitride will be obtained from H. C. Starck Company. At present, we are assessing different procedures for homogenization and sample preparation from these powders.

Status of milestones

Milestone 411514 [Finalize research plans on subtasks 7 and 8 (depending on Executive Committee approval)] was completed at the Executive Committee meeting on October 6, 1993.

Milestone 411515 - Order U.S. ceramic material for IEA Annex II, subtask 7, was completed on January 31, 1994.

Other milestones are on schedule.

Communications/visits/travel

V. J. Tennery attended the IEA Executive Committee Meeting in Stuttgart, Germany, on October 6, 1993. He also attended the conference, "Silicon Nitride '93," at the Max-Planck Institute for Metals Research and visited several German laboratories.

There were several communications on the details of subtask 7 - see above.

Publications and Presentations

"Research and Development Activities in the High Temperature Materials Laboratory," V. J. Tennery, presented at Hoechst AG, Materials Research, Frankfurt, Germany, September 30, 1993.

"IEA Annex II Subtask 5 Summary of United States Results," Executive Committee Meeting, presented by V. J. Tennery, Stuttgart, Germany, October 6, 1993.

"IEA Annex II, Subtask 7 Proposed Work, Executive Committee Meeting," presented by V. J. Tennery, Stuttgart, Germany, October 6, 1993.

The following reports were received and distributed to the U.S. participants:

"Mechanical Characterization of Engineering Ceramics - IEA ANNEX II Subtask 5," A. Brückner-Foit,¹ W. Berweiler,² T. Hollstein,² A. Mann,¹ D. Munz,¹ and K. Schirmer,¹ September 1993.

"Report on Mechanical Evaluation of Advanced Ceramics within IEA, Subtask 5 - Japanese Final Report," Mineo Mizuno and Yasuo Nagano, Japan Fine Ceramics Center, November 1993.

"Mechanical Characterization and Fractographic Investigations of Silicon Nitride, IEA Annex II, Subtask V - Swedish Summary Report," Lennart Carlsson, Swedish National Testing and Research Institute, Borås, Sweden, September 1993.

¹Institut für Zuverlässigkeit und Schadenskunde im Maschinenbau, Universität Karlsruhe, Karlsruhe, Germany.

²Fraunhofer-Institut für Werkstoffmechanik, Freiburg, Germany.

Characterization of Ceramic Powders

S. G. Malghan and L.-S. Lum

(National Institute of Standards and Technology)

Objective/Scope

Ceramics have been successfully employed in engines on a demonstration basis. The successful manufacture and use of ceramics in advanced engines depends on the development of reliable materials that will withstand high, rapidly varying thermal stress loads. Improvement in the characterization of ceramic starting powders is a critical factor in achieving reliable ceramic materials for engine applications. The production and utilization of such powders require characterization methods and property standards for quality assurance.

The objectives of the NIST program are: (1) to assist with the division and distribution of ceramic starting powders for an international round-robin on powder characterization; (2) to provide reliable data on physical (dimensional), chemical and phase characteristics of powders; and (3) to conduct statistical assessment, analysis and modeling of round-robin data. This program is directed toward a critical assessment of powder characterization methodology and toward establishment of a basis for the evaluation of fine powder precursors for ceramic processing. This work will examine and compare by a variety of statistical means the various measurement methodologies employed in the round-robin and the correlations among the various parameters and characteristics evaluated. The results of the round-robin are expected to provide the basis for identifying measurements for which Standard Reference Materials are needed and to provide property and statistical data which will serve the development of internationally accepted standards.

Technical Progress

The primary activities during this reporting period were preparation for the IEA Executive Committee Meeting, procedures development for Subtask 8, analysis of participants feedback, and collection of powders.

The IEA Annex 2 Executive Committee Meeting was held in Stuttgart, Germany on October 8, 1993 in conjunction with Silicon Nitride 93 Conference. The primary agenda items concerning this activity were the release of Subtask 6 final report and presentation of Subtask 8 technical plan. S. G. Malghan made two presentations on Subtasks 6 and 8. The Subtask 6 presentation constituted major conclusions and recommendations, benefits to participants, and an overview of the final report. In addition to two data compilation reports, the results of Subtask 6 activities were presented in the form of two reports: one was an interim report on procedures compilation; and the second was the final report containing all data, procedures, data analysis, discussion of results, conclusions, and recommendations. This is the first of its kind of reports which brings together a large body of reliable data and procedures. It is intended that the participants in all four countries will use these procedures in their laboratories. In fact, a number of

participants have been already utilizing these procedures. It is likely that in future years these procedures may be improved as new data and understanding is developed. But for now, they represent the best effort, consensus based procedures for analysis of ceramic powders.

The Subtask 8 presentation constituted a description of technical plan, powders selection and participants. The technical plan consists of developing and testing procedures for the measurement of primary and secondary properties of powders. The focus of procedures development for primary properties is on sample dispersion, dissolution and use of appropriate standard reference materials in order to improve accuracy and intermethod comparison of data. We plan to study silicon nitride and silicon carbide as primary powders. In addition, alumina, zirconia, and aluminum nitride will be studied as optional powders. A suggestion was made by technical leaders to include a silicon nitride powder made by gas phase reaction as an optional powder so that the procedures will be equally applicable to powders having highly divergent properties. This matter was discussed with participants through a questionnaire.

At present, 35 participants are involved in this activity, including two from Belgium and one from Norway. The executive committee allowed the participation of Belgium and Norway to continue until a final decision can be reached at a later stage.

A major decision affecting ASTM powder procedures development activity was reached at this executive committee meeting. The committee voted to release the reports to the standards setting bodies in the participating countries. This decision has an important bearing on the ASTM C-28.05 activities. We can now write a number of draft standards based on the procedures and supporting data contained in the Subtask 6 final report. This item was discussed at the January 1994 ASTM C-28.05 meeting in Cocoa Beach.

We are continuing to develop, revise, and test procedures for characterization of secondary properties of powders. At present, we have a few procedures that have been tested using alumina as a candidate powder. The A-16 alumina, one of the optional powders, is being used since it is readily available. The testing involves primarily the evaluation of major parameters affecting the robustness of the procedure and effects of the measurement parameters on the response. Some of the procedures that have undergone testing are deagglomeration by ultrasonication, settling behavior, and agglomerate size distribution in the measurement of dispersion. In addition, in the preparation of slurry, the procedures for the measurement of slurry pH, sedimentation, and casting rate have been tested.

A procedure for the determination of agglomerates size distribution has been developed and tested at NIST. This procedure has been found to provide a fairly repeatable data. The testing of this procedure has been completed primarily by using an alumina powder. Applicability of this procedure to other powders will be evaluated shortly.

Regarding the procurement of primary and optional powders, we need at least twenty five kilograms each of these powders.

We have purchased a 25 kg batch of UBE SNE-10 silicon nitride powder from Ube Industries. In addition, samples of alumina and aluminum nitride powders have been provided by Alcoa and Dow Chemical Company,

respectively. The zirconia powder will be supplied by Japan Fine Ceramic Center, Japan; while silicon carbide and gas phase silicon nitride powders will be obtained from H.C. Starck Company. At present, we are assessing different procedures for homogenization and samples preparation of these powders.

At the Cocoa Beach ASTM meeting, the C-28.05 sub-committee discussed a number of issues. At present, one procedure on specific surface area has passed the main committee ballot and two more are nearing completion for resubmission. Several editorial comments were suggested for the drafts on particle size measurement by sedimentation and centrifugal sedimentation. These two drafts will be revised and submitted for the final ballot. Subsequent to the decision by the IEA Annex 2 executive committee, the Subtask 6 final report was made available to the committee members interested in using the report to develop draft standards. Four participants have agreed to undertake this task.

A standard reference material (SRM) on particle size measurement of zirconia powder was developed. This SRM is useful in the calibration of x-ray sedimentation instruments in the one micrometer range. The procedure used in the certification of this SRM was partly based on that developed for the IEA Subtask 6 at NIST. This SRM can be purchased from the NIST Office of Standard Reference Materials.

Technical leaders in Japan and Germany have held meetings with their participants to review progress and reach a consensus on powders selection and work distribution. Subsequently, Dr. Naito, Japan's technical leader visited NIST to coordinate with the primary effort. During a week-long meeting, several subjects including feedback from Japan's participants meeting, standardization activities in Japan, and preliminary comments on procedures were discussed.

A meeting of the US participants will be held in May to discuss procedures and powders preparation methods. The current participants in Subtask 8 are Alsimag, Golden Technologies, Garrett Ceramic Components, Dow Chemical Company, NIST, Ceramic Process Systems, St. Gobain/Norton Company, and W.R. Grace Company.

Inputs from a significant number of participants with respect to their selection of powders have been analyzed. It appears that all six powders proposed at the Stuttgart meeting in Germany have been retained for study. In addition, the participants in Japan would like to study a number of primary properties of secondary powders (alumina, zirconia, and aluminum nitride). Dr. Naito has agreed to collect the procedures for analysis of primary properties of these powders.

Status of Milestones

On target.

Publications/Presentations

Final report on IEA Subtask 6 was released to participants.

Communications/Visits

Dr. Naito, technical leader of Japan for Subtask 8 and Mr. Hosakawa, Japan Fine Ceramics Center visited NIST for Subtask 8 discussions.

Ceramic Mechanical Property Test Method Development

George D. Quinn

(National Institute of Standards and Technology)

Objective/Scope

This is a new task with a focus on developing mechanical test method standards in support of the Ceramic Technology for Advanced Heat Engines and Advanced Turbine Technology Applications Programs. The prime DOE contractors and subcontractors will be surveyed by on-site visits to assess their needs and capabilities. Test method development should also consider the general USA structural ceramics community as well as foreign laboratories and companies, but emphasis will be placed on the needs of the DOE community.

Draft recommendations for practices or procedures shall be developed based upon the needs identified above and circulated within the DOE ceramics heat engine community for review and modification. Round robins will be conducted as necessary, but shall be well-focussed, limited in scope and not interfere with ongoing IEA round robins. Procedures developed in this program shall be presented as ATTAP or CTAHE "standard procedures." Alternatively, (and eventually) these will be advanced for final standardization by ASTM or by the U.S. Army as possible MIL STD's.

Technical Highlights and Results

Previous work in this project has contributed to the following completed standards:

1. ASTM C-1198-91 "Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Sonic Resonance," by S. Gonczy, Allied-Signal; G. Quinn, NIST; and J. Helfinstine, Corning.
2. ASTM C-1161-90 "Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature," G. Quinn, NIST.
3. ASTM C-1211-92 "Standard Test Method for Flexural Strength of Advanced Ceramic at Elevated Temperature," by G. Quinn in cooperation with Mr. M. Foley, Norton; Mr. T. Richerson, Allied-Signal; and Dr. M. Ferber, ORNL.
4. MIL HDBK 790 "Fractography and Characterization of Fracture Origins in Advanced Structural Ceramics," with J. Swab and M. Slavin, U. S. Army, ARL.
5. ASTM C-1239-93 "Standard Practice for Reporting Strength Data and Estimating Weibull Distribution Parameters," by S. Duffy, NASA-Lewis; G. Quinn, NIST; and C. Johnson, G.E.

Weibull Analysis

The document: "Reporting Uniaxial Strength Data and Estimating Weibull Distribution Parameters for Advanced Ceramics," by S. Duffy, G. Quinn, and C. Johnson was accepted as an ASTM standard practice and designated C-1239. A few minor revisions need to be made to this document, and supplemental ballot and revisions will be undertaken in late 1993 and early 1994 as needed. A few follow-up matters are also

being tended to. In particular, we are monitoring and corresponding with key personnel in Europe who are preparing an analogous European (CEN) standard. As much as possible, we wish to keep these standards harmonious and consistent with each other.

Fracture Toughness

Standardization of fracture toughness testing continues. Mr. Jonathan Salem of NASA-Lewis is the overall leader of this activity. Professor Isa Bar-on of Worcester Polytechnic Institute is acting as the C-28 - E-8 committee liaison.

During this 6 months period, there was intensive work at NIST on analyzing the results of the surface crack in flexure round-robin. This VAMAS project started in November 1992 and ended in September 1993. The round-robin was a joint program by NIST and by EMPA, the Swiss Federal Research Laboratory. Twenty-four laboratories in Europe and the United States participated, of which 20 returned results in the allotted time. In the US, the participants were NASA-Lewis, NIST, and Alfred University. The round-robin involved three materials: Norton hot-pressed silicon nitride, grade NC 132; ESK hipped silicon nitride; and EMPA (Swiss) sintered yttria-partially stabilized zirconia. The latter two materials were donated by EMPA.

Much time during this semiannual period was spent in documenting the results in cooperation with Mr. Kübler of EMPA who stayed at NIST from May-November 1993. A draft final report was ready in December and was thoroughly reviewed by all twenty participating labs. Revisions have been made and the final report is being reviewed internally at NIST. In the meantime, summary results have been presented at the ASTM C-28, VAMAS TWA #3, and American Ceramic Society meetings at Cocoa Beach in January 1994.

Figures 1 through 3 illustrate the fracture toughness results. Excellent consistency was obtained for the NC-132 hot-pressed silicon nitride. All 20 laboratories reported results. The grand average toughness for 107 accepted specimen was 4.6 MPa/m with a standard deviation of only 0.4. The ESK silicon nitride was more difficult to test, and the average toughness for 105 accepted specimens was 5.0 MPa/m with a standard deviation of 0.6. Only 12 laboratories tried the zirconia, which was optional, and eight laboratories obtained accepted results with an average for 37 specimens of 4.5 MPa/m and a standard deviation of 0.6. The zirconia posed many problems for the laboratories, and several misinterpreted their fracture surfaces and marked hackle lines as the precrack. This data is shown in Figure 3 but is marked by an "X" and is not included in the grand average.

In the case of NC-132, the average is in excellent agreement with chevron notch (CN) and single-edged precracked beam (SEPB) results obtained at NASA-Lewis by Shannon and Salem. A review of over 20 studies that have published fracture toughness values for NC-132 indicates that a value of 4.6 probably is the definitive toughness for this material. The ESK and zirconia results are credible as well, but there is fewer alternative data to compare the results to. A similar outstanding agreement of CSF to CN and SEPB data had been reached earlier on sintered α silicon carbide (Carborundum SA), published by Ghosh, Bradt, Kobayashi, Jenkins and Salem at U. Washington.

Figure 1. Results of the fracture toughness by the controlled surface flaw method for NC-132 hot-pressed silicon nitride. The average and standard deviation of each laboratory's results are shown as well as the number of specimens the laboratory had some success with. Laboratories usually tried either 5 or 10 specimens. The grand average is shown by the dotted line.

Figure 2. Results for the ESK hipped silicon nitride, which was more difficult than the NC-132.

Figure 3. Results for the yttria-stabilized tetragonal zirconia (Y-TZP). Of 12 laboratories that attempted this material, eight had some measure of success.

A stunning conclusion from the round-robin is that the results are not sensitive to the details of the precrack size measurement. It is true that the participants had different tendencies and inclinations in marking and measuring their precracks, but there is a mitigating influence of the square root dependence of fracture toughness upon the precrack size. Fracture toughness, K_{Ic} , by this method is calculated:

$$K_{Ic} = Y \sigma \sqrt{a}$$

where σ is the flexure stress, a is the semiellipse depth, and Y is a stress intensity shape factor. There was a remarkable tendency for the Newman-Raju stress intensity shape factors (Y) to partially-offset the scatter in the crack size measurements. That is to say, an overestimate in precrack depth measurement, a , was *offset by a change in the Y factor*. For example, in some instances a 10% error in the " a " measurement led to *less than 1% error in K_{Ic}* . This helps to explain why the respondents were able to obtain similar results despite very different procedures and criteria for measuring the precrack size. This interplay of " Y " and " a " had not been appreciated in the technical community since average Y factors had been used in the past. In the present round robin, the Y factor for each and every precrack was computed by means of a spreadsheet which had the complicated Newman-Raju factors programed in to the cells.

In fact, some participants sent precrack size measurements which we suspect were not properly calibrated. For example, the indicated nominal magnification of the scanning electron microscope was used, despite the fact these magnifications may have 10% error. Nonetheless, the results they obtained are in fair to good agreement with those of other labs.

The success of this exercise indicates that the SCF method warrants standardization. It was not clear whether this was so at the beginning of the exercise, since there was a serious concern over some aspects of the method, such as whether the participants could read the precracks properly. There is a new impetus to use this method since a new ASTM standard for metals, E-740, uses a method that is conceptually very similar. The findings of the round-robin exercise will be used to refine new ceramic fracture toughness standard being developed in ASTM Committees C-28 and E-8. This draft features the surface crack in flexure, the chevron notch, and the single-edged precracked beam methods.

One element of the proposed draft standard is the number of specimens needed. Whereas 30 or more specimens are needed for flexure strength measurements, we hope that a far fewer are necessary for fracture toughness. Prof. Bar-on of Worcester Polytechnic had proposed that as few as 4 specimens would suffice. This estimate seemed small, so NIST studied this matter in more detail using the data from the SCF round robin. The data base of 107, 105, and 37 specimens for the three materials tested represents one of the largest data bases ever accumulated on advanced ceramics *for a specific set of test conditions*. It was determined that the fracture toughness values are normally (Gaussian) distributed and that the scatter within and between labs can be analyzed with conventional, simple statistical methods.

Thus, the scatter in mean values for toughness from lab to lab (reproducibility in ASTM parlance) can easily be interpreted by the application of the central limit theorem. This states that the lab mean fracture toughness will scatter about a population mean, with a standard deviation equal to the population standard deviation divided by the square root of the sample size (number of specimens). This very simple relationship can be used to give confidence intervals on deviations of a lab mean from the population mean. The deviation is *independent of the mean toughness, and only depends on the scatter in toughness values and the sample size*. We can conclude that 4 specimens are adequate, since the improvement in the confidence bounds is negligible in going from 4 to 5 specimens (a mathematical difference between $\sqrt{4}$ to $\sqrt{5}$), and may not be worthwhile in going to as many as 10 specimens. This conclusion is borne out by the data from the round robin, Figures 1-3, which indicates that most labs obtained the mean toughness values near the population mean with sample sizes as few as 4 or 5 specimens!

Additional experiments on the zirconia in an inert atmosphere were conducted at NIST in October. This was carried out in an attempt to distinguish R-curve behavior as distinct from environmentally-assisted slow crack growth. Both phenomena interfere with attempts to measure a single fracture toughness value, and the ASTM draft standard must take this into account.

A billet of NC-132 was given by G. Quinn to J. Salem in October 1993 to enable NASA-Lewis to run a chevron notch round-robin on this material.

Hardness

Work has continued at NIST on developing hardness standards for advanced ceramics. An internally funded program is attempting to develop two "standard reference materials, SRM" for which the hardness is certified by NIST. On the basis of a review of ceramic hardness data, it was determined that there is a need for Vickers and a Knoop hardness SRM and standard test methods.

Hardness testing in principal is very simple, but in practice results are very sensitive to the technique. Our original intent was to simply modify current techniques and write a simple standard for advanced ceramics. ASTM standards C 730 for glasses and C 849 for whitewares would have been used, but these were prepared in the early 1970's, and new information has come to light that must be considered. For example, a VAMAS round robin in the late 1980's produced new information on the accuracy, repeatability, and reproducibility of ceramic hardness measurements. The biggest problem with measuring the hardness of advanced ceramics is that since the materials are themselves hard, the indentations are very small. It is difficult to get a precise or accurate reading of the diagonal length with an ordinary microscope. Operator bias and technique are critical factors. Draft #2 of an advanced ceramic, Knoop hardness standard was presented at the C-28 meeting in January 1994, but it was noted that several technical problems remained. These have been resolved during this semiannual period.

It was decided that work will initially focus on a Knoop standard since there are already two related ASTM standards as noted above. During this semiannual period, we carefully studied the matter of the apparent shortening of the diagonal lengths due to the limits of resolution of optical microscopes as illustrated in Figure 4. The $7\lambda/2NA$ correction factor is mandated in the two ASTM standards C-730 and C-849, but is not used by standards in the rest of the world. The difference in hardness with or without the correction factor is about 100-150 units for most glasses! This has led to wild confusion in the literature with respect to whether the correction factor has or has not been applied. For example, older versions of the Schott Glass catalog list the hardness with and without the factor. The original work which suggested the necessity of correction factor was done in the 1950's, before the advent of scanning electron microscopy. We therefore measured indentations with several optical microscopes and with a calibrated scanning electron microscope in order to verify the effect. The result of this exercise, plus a complete review of the technical literature, suggests that the $7\lambda/2NA$ correction factor is an *overestimate* of the correction needed. We noted that our best calibrated scanning electron microscope measurements added only 0.6 - 1.2 micrometers to the lengths of Knoop impressions in hot-isopressed silicon nitride, not the 3.0 micrometers predicted by the $7\lambda/2NA$ correction factor. This conclusion is on the basis of repeated measurements by NIST and also comparisons with the data furnished in the round robin described below.

Similar comparisons for the Vickers indentations indicated that there is negligible difference between the SEM measurements and optical readings. There is less of an optical resolution problem with Vickers indents since the corners are clearer to discern and are not long, slender, tapered tips in the Knoop impressions.

During this 6 months period, a small round-robin was set up (October 1993), conducted (November-December), and completed (January 1994). Participants measured the hardness of a steel ball, a tungsten carbide disk, and a silicon nitride ball. Eight laboratories participated: Cerbec, Corning, Osram/Sylvania, ORNL, Wilson, Kennametal, NPL-England, and MPA-Dortmund, Germany. The latter two are world leaders in hardness testing. Results from this exercise verified that the prototype SRM were suitable, and furthermore furnished information about repeatability and reproducibility that can be used for a precision and bias statement in an ASTM standard.

Now that the technical problems have been resolved, and precision and accuracy data are available, we will proceed to prepare a ballot-ready draft standard on test methods for Knoop and Vickers hardness and present them to C-28 Committee in June 1994 in Montreal.

Fractography

During this 6 months period, additional elements of MIL HDBK 790, "Standard Practice for Characterizing Fracture Origins Limiting Defects in Advanced Structural Ceramics" were brought into the ASTM C-28 forum. This work is a collaborative undertaking with NIST and with J. Swab of U. S. Army Research Laboratory (ARL). A list of flaw definitions was introduced into the Terminology Subcommittee, C- 28.91 and these were

OPTICAL RESOLUTION LIMITS

The least distance separable
by a given objective is:

$$\lambda/(2NA)$$

VICKERS

$$\lambda/(2NA)$$

$$\lambda/(4NA)$$

$$\text{both ends: } \lambda/(2NA) = .55 \mu\text{m}/(2 \cdot .65) = 0.4 \mu\text{m}$$

KNOOP

$$\lambda/(2NA)$$

$$7\lambda/(4NA)$$

$$\text{both ends: } 7\lambda/(2NA) = 7 \cdot .55 \mu\text{m}/(2 \cdot .65) = 3.0 \mu\text{m!}$$

Figure 4. The limits of resolution of an optical microscope lead to an underestimate of the indentation diagonal length. The problem is more pronounced in Knoop indentations. A 3 micrometer long impression can occur with a 40X objective lens with a numerical aperture (NA) of 0.65. This 10% underestimate of length lead to a 20% hardness error.

balloted in September 1993. A number of negative ballots were obtained, as well as some constructive comments on affirmative comments. These were discussed at the January 1994 C-28 Cocoa Beach meeting.

In the meantime, a fractography round-robin was organized under the auspices of the VAMAS collaboration and completed. This exercise was developed by the US ARL in cooperation with NIST. Emphasis was on the detection and characterization of machining damage, the detection and characterization of material processing related flaws, and fractographic techniques and analysis. The round-robin will include the examination of photos and specimens. The US (ARL) distributed the photos and specimens in May 1993 and the exercise closed out in October. NIST is assisting with the interpretation of these results. Preliminary conclusions were presented at ASTM C-28, VAMAS TWA #3, and American Ceramic Society meetings at Cocoa Beach in January 1994.

Status of Milestones

- 412118 Prepare final draft of surface crack in flexure portion of draft ASTM C-28 standard. Delayed from January 1994 to June 1994 due to the additional time needed to analyze and write up the VAMAS round robin results.
- 412130 Prepare preliminary draft of a Vickers hardness standard test method for ASTM C-28. Delayed from January 1994 to June 1994 due to additional time needed to analyze hardness round robin results and to solve the matter of optical resolution limits.

All other milestones are on schedule.

Communications/Visits/Travel

1. G. Quinn and R. Gettings attended the American Ceramic Society, VAMAS, and ASTM C-28 meetings in Cocoa Beach, FL in January 1994.
2. G. Quinn assisted Golden Technologies in determining the source of a flexure strength testing problem connected with their DOE sponsored program.
3. G. Quinn visited the National Physical Laboratory in London following a VAMAS meeting in order to discuss their hardness standardization projects and to review their long history of working in the field. The points of contact were Dr. R. Morrell and Dr. R. Peggs.
4. Numerous correspondence and telephone conversations occurred in connection with the hardness, fracture toughness, and fractography round robins.
5. Mr. J. Swab visited NIST to review and coordinate the analysis of the fractography round robin results.

6. G. Quinn prepared an extensive, 10 page review of a draft flexure strength of ceramic composites standard written by Dr. S. Gonczy of Allied Signal.
7. G. Quinn contacted Dr. H. Richter of Cerasiv and Dr. T. Polzin of MPA Dortmund in Germany in order to discover details of a small German round robin on hardness testing. The Germans agreed to allow NIST participation in this round robin.
8. G. Quinn contacted Mr. H. Hagy of Corning in connection with ASTM Committee C-14 (Glass) standard C-730. Close contact will be maintained in order to keep the C-28 and C-14 standards for hardness in harmony.
9. A detailed letter was sent by G. Quinn to Committee F-04 on Medical and Surgical Devices regarding a draft specification for zirconia for artificial prostheses. The draft contained a sketchy outline of a fracture toughness procedure.
10. Information about several European round robins and formal standards dealing with dynamic fatigue was given to Mr. J. Salem and S. Choi of NASA-Lewis in the hopes that this would help their effort to write an ASTM standard on this topic. G. Quinn obtained special permission from Europe to release this information.
11. A number of conversations were held with key personnel regarding the new ISO (International Standard Organization) Committee on Fine Ceramics, the secretariat for which is held by Japan. An ASTM C-28 policy was developed at the C-28 meeting in Cocoa Beach and in subsequent correspondence and telephone conversations. A formal reply to a Japanese questionnaire was prepared. Mr. Edward Anderson of Alcoa will represent the United States in ISO TC 206.
12. G. Quinn reviewed a draft test method for "C" ring testing that Dr. A. Segall at Penn State prepared for C-28.
13. G. Quinn attended the Contractor's Coordination Meeting in Dearborn in October.

Publications/Presentations

1. ASTM Standard C-1239-93 "Standard Practice for Reporting Strength Data and Estimating Weibull Distribution Parameters," by S. Duffy, NASA-Lewis; G. Quinn, NIST; and C. Johnson, G.E., ASTM Annual Book of Standards, 1994.
2. G. Quinn, R. Gettings, and J. Kübler, "Fracture Toughness by the Surface Crack in Flexure (SCF) Method: Results of the VAMAS Round Robin," presented at the ACS meeting, Cocoa Beach, Jan. 1994, to be publ. Ceram. Eng. and Sci. Proc. 1994.
3. J. J. Swab, and G. Quinn, "Results of a Round Robin Exercise on the Fractography of Advanced Structural Ceramics," *idem*.

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